Supporting Information

Modular Assembly of Aldehydes, Styrenes and CO_2 for the Synthesis of γ-Hydroxy Acids under Organophotocatalysis

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1. Supplementary Methods

All new compounds were fully characterized. NMR spectra were recorded on Bruker Avance II 400, Vaian DLG400, Bruker AVANCE III 500. NMR Spectroscopy and calibrated using residual undeuterated solvent ($CDCl_3$ = 7.26 ppm or TMS = 0 ppm ^1H NMR, 77.16 ppm ^{13}C NMR). Mass spectra were conducted at Thermo LTQ Orbitrap XL (ESI).

Anhydrous solvents, such as Dimethylacetamide (DMA), *N*, *N*, *N*, *N*-Dimethylformamide (DMF), Acetonitrile (MeCN), *N*-Methylpyrrolidone (NMP), Dimethyl sulfoxide (DMSO), Tetrahydrofuran (THF), Dichloromethane (DCM), Ethyl acetate (EA) were purchased from *J&K* Scientific. XAT reagent, such as *N, N, N, N*-Tetramethylethylenediamine (TMEDA), *N, N*-Diisopropylethyl amine (DIPEA), *N, N*-Diisopropylethy lamine (DIPEA), Triethylamine (Et_3N), *N, N*'-Dimethyl-1,2-ethanediamine (DMEDA), Dicyclohexylamine (Cy_2NH), 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), *N, N*-Dimethylaniline ($PhNMe_2$), Diisopropylamine (IPr_2NH), *N, N*-dimethylaniline ($PhNMe_2$), Tris(trimethylsilyl)silane ($(TMS)_3SiH$) were obtained from commercial suppliers. Photocatalysts was purchased from Adamas-beta or synthesized according to the procedures outlined below. CO_2 gas was purchased from Dalian Guangming Special Gas Co., Ltd (purity: 99.99%) and used as received. Flash column chromatography was carried out using silica gel (General-Reagent, AR, 200-300 mesh, for column chromatography). Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. PE represents petroleum ether.

All photoredox reactions were performed with an RLH-18CU full spectrum LED control box and RLH-18HC-B heating stirring base (Figure S1), which was purchased from Beijing Roger tech Ltd. The reaction system was equipped with eight blue light LEDs and a low temperature coolant circulating pump to keep the reaction temperature at –10 °C.

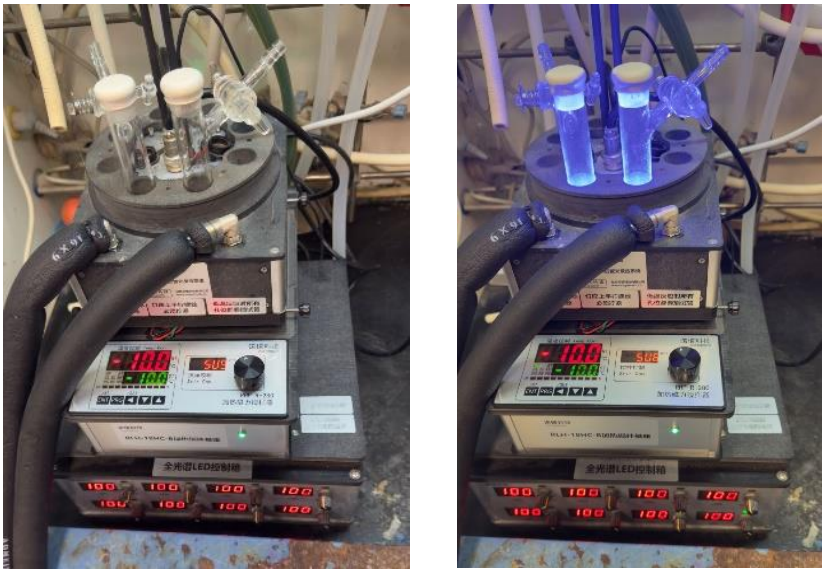
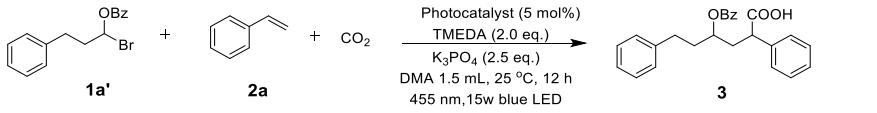
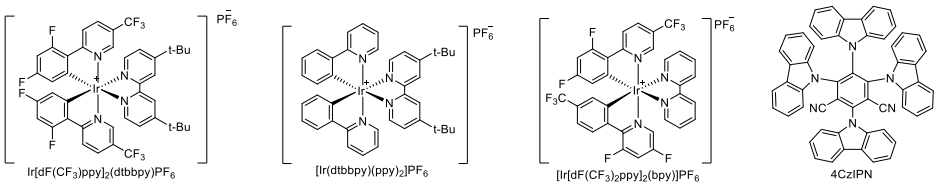
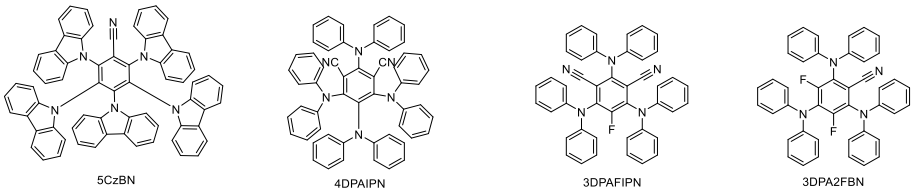


Figure S1. Photoreaction setup

2. Optimization of reaction conditions







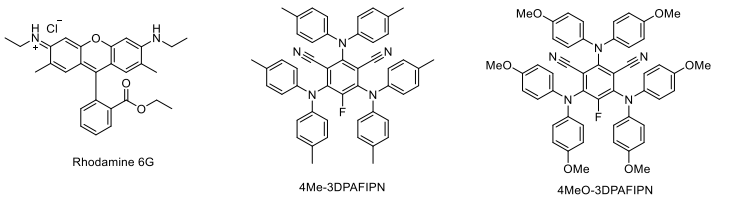


Table S1. Exploration of photocatalyst [a]

Entry	Photocatalyst	Yield of **3** (%)
1	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	10
2	$[Ir(dtbbpy)(ppy)_2]PF_6$	N.D.
3	$[Ir[dF(CF_3)_2ppy]_2(bpy)]PF_6$	N.D.
4	4CzIPN	12
5	5CzBN	26
6	4DPAIPN	28
7	3DPAFIPN	50
8	3DPA2FBN	N.D.
9	Rhodamine 6G	12
10	3DPAFIPN-Me	40
11	3DPAFIPN-OMe	N.D.

[a]Reaction conditions: **1a'** (0.1 mmol, 1.0 eq.= 1.0 equivalent), **2a** (0.15 mmol, 1.5 eq.), photocatalyst (0.005 mmol, 5 mol%), K_3PO_4 (0.25 mmol, 2.5 eq.), TMEDA (0.2 mmol, 2.0 eq.), DMA (1.5 mL), CO_2 (1 atm), 455 nm 15W blue LEDs, 25 °C, 12 h. [b]Yields were determined by ^1H NMR with CH_2Br_2 (7 μL, 0.1 mmol) as an internal standard. N.D. not determined.

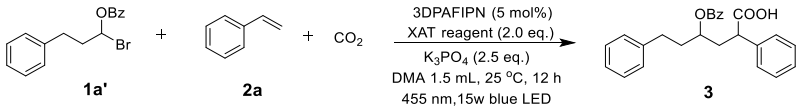


Table S2. Exploration of XAT reagent [a]

Entry	XAT reagent	Yield of **3** (%)
1	TMEDA	50
2	DIPEA	30
3	Et_3N	38
4	DMEDA	30
5	DABCO	N.D.
6	Cy_2NH	34
7	DBU	N.D.
8	$PhNMe_2$	40
9	IPr_2NH	34
10	$PhNMe_2$	40
11	$(TMS)_3SiH$	22

[a]Reaction conditions: **1a'** (0.1 mmol, 1.0 eq.), **2a** (0.15 mmol, 1.5 eq.), 3DPAFIPN (0.005 mmol, 5 mol%), K_3PO_4 (0.25 mmol, 2.5 eq.), XAT reagent (0.2 mmol, 2.0 eq.), DMA (1.5 mL), CO_2 (1 atm), 455 nm 15W blue LEDs, 25 °C, 12 h. [b]Yields were determined by ^1H NMR with CH_2Br_2 (7 μL, 0.1 mmol) as an internal standard. N.D. not determined.

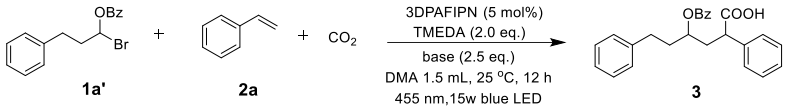


Table S3. Exploration of base [a]

Entry	Base	Yield of **3** (%)
1	K_3PO_4	50
2	/	44
3	Cs_2CO_3	46
4	t-BuOK	34
5	Na_2CO_3	46
6	K_2CO_3	40
7	K_2HPO_4	38
8	CH_3ONa	20

[a]Reaction conditions: **1a'** (0.1 mmol, 1.0 eq.), **2a** (0.15 mmol, 1.5 eq.), 3DPAFIPN (0.005 mmol, 5 mol%), base (0.25 mmol, 2.5 eq.), TMEDA (0.2 mmol, 2.0 eq.), DMA (1.5 mL), CO_2 (1 atm), 455 nm 15W blue LEDs, 25 °C, 12 h. [b]Yields were determined by ^{1}H NMR with CH_2Br_2 (7 μL, 0.1 mmol) as an internal standard.

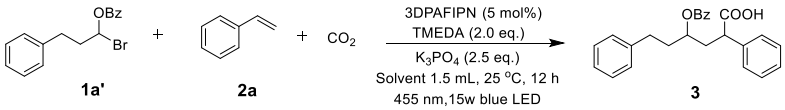


Table S4. Exploration of solvent [a]

Entry	Solvent	Yield of **3** (%)
1	DMA	50
2	DMF	46
3	CH_3CN	20
4	NMP	34
5	DMSO	6
6	THF	14
7	DCM	18
8	EA	N.D.
9	Acetone	26
10	Toluene	N.D.

[a]Reaction conditions: **1a'** (0.1 mmol, 1.0 eq.), **2a** (0.15 mmol, 1.5 eq.), 3DPAFIPN (0.005 mmol, 5 mol%), K_3PO_4 (0.25 mmol, 2.5 eq.), TMEDA (0.2 mmol, 2.0 eq.), solvent (1.5 mL), CO_2 (1 atm), 455 nm 15W blue LEDs, 25 °C, 12 h. [b]Yields were determined by ^{1}H NMR with CH_2Br_2 (7 μL, 0.1 mmol) as an internal standard. N.D. not determined.

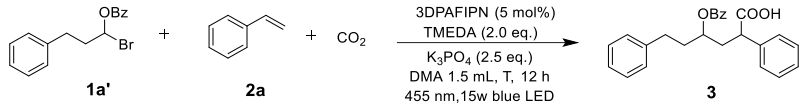


Table S5. Exploration of temperature[a]

Entry	Temperature (°C)	Yield of **3** (%)
1	25	50
2	15	54
3	5	62
4	0	66
5	–5	68
6	–10	70
7	–15	68

[a]Reaction conditions: **1a'** (0.1 mmol, 1.0 eq.), **2a** (0.15 mmol, 1.5 eq.), 3DPAFIPN (0.005 mmol, 5 mol%), K_3PO_4 (0.25 mmol, 2.5 eq.), TMEDA (0.2 mmol, 2.0 eq.), DMA (1.5 mL), CO_2 (1 atm), 455 nm 15W blue LEDs, T, 12 h. [b]Yields were determined by ^1H NMR with CH_2Br_2 (7 μL, 0.1 mmol) as an internal standard.

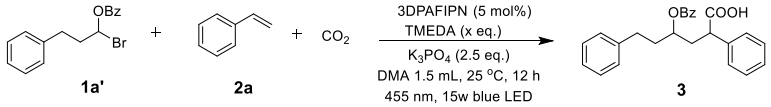


Table S6. Exploration of TMEDA equivalent [a]

Entry	TMEDA (eq.)	Yield of **3** (%)
1	1.0	66
2	2.0	70
3	3.0	72
4	4.0	70
5	5.0	68

[a]Reaction conditions: **1a'** (0.1 mmol, 1.0 eq.), **2a** (0.15 mmol, 1.5 eq.), 3DPAFIPN (0.005 mmol, 5 mol%), K_3PO_4 (0.25 mmol, 2.5 eq.), TMEDA (x eq.), DMA (1.5 mL), CO_2 (1 atm), 455 nm 15W blue LEDs, –10 °C, 12 h. [b]Yields were determined by ^1H NMR with CH_2Br_2 (7 μL, 0.1 mmol) as an internal standard.

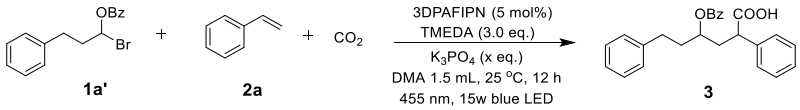


Table S7. Exploration of base equivalent [a]

Entry	base equivalent (eq.)	Yield of **3** (%)
1	/	70
2	0.5	72
3	1.0	74

Entry	base equivalent (eq.)	Yield of **3** (%)
4	1.5	74
5	2.0	72
6	2.5	72
7	3.0	70

[a]Reaction conditions: **1a'** (0.1 mmol, 1.0 eq.), **2a** (0.15 mmol, 1.5 eq.), 3DPAFIPN (0.005 mmol, 5 mol%), K_3PO_4 (x eq.), TMEDA (3.0 eq.), DMA (1.5 mL), CO_2 (1 atm), 455 nm 15W blue LEDs, –10 °C, 12 h. [b]Yields were determined by ^1H NMR with CH_2Br_2 (7 μL, 0.1 mmol) as an internal standard.

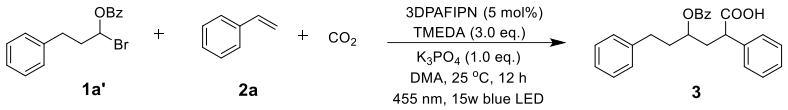


Table S8. Exploration of reactant concentration [a]

Entry	DMA (mL)	Yield of **3** (%)
1	0.5	66
2	1.0	74
3	1.5	74
4	2.0	74
5	2.5	70

[a]Reaction conditions: **1a'** (0.1 mmol, 1.0 eq.), **2a** (0.15 mmol, 1.5 eq.), 3DPAFIPN (0.005 mmol, 5 mol%), K_3PO_4 (1.0 eq.), TMEDA (3.0 eq.), DMA, CO_2 (1 atm), 455 nm 15W blue LEDs, –10 °C, 12 h. [b]Yields were determined by ^1H NMR with CH_2Br_2 (7 μL, 0.1 mmol) as an internal standard.

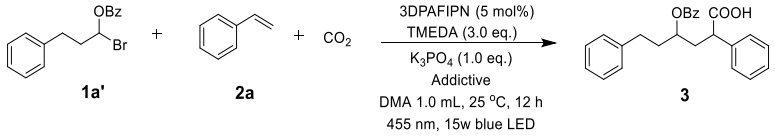


Table S9. Exploration of addictive [a]

Entry	additive	Yield of **3** (%)
1	/	74
2	5 Å MS (50 mg)	76
3	5 Å MS (75 mg)	74
4	5 Å MS (100 mg)	74

[a]Reaction conditions: **1a'** (0.1 mmol, 1.0 eq.), **2a** (0.15 mmol, 1.5 eq.), 3DPAFIPN (0.005 mmol, 5 mol%), K_3PO_4 (1.0 eq.), TMEDA (3.0 eq.), DMA (1.0 mL), 5 Å MS, CO_2 (1 atm), 455 nm 15W blue LEDs, –10 °C, 12 h. [b]Yields were determined by ^1H NMR with CH_2Br_2 (7 μL, 0.1 mmol) as an internal standard.

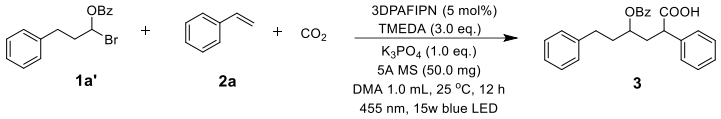


Table S10. Optimization of the ratio between **1a'** and **2a** [a]

Entry	**1a':2a**	Yield of **3** (%)
1	1 : 1.5	76
2	1 : 2	76
3	1 : 2.5	78
4	1 : 3	80
5	1 : 3.5	80
6	2 : 1	52

[a]Reaction conditions: **1a'** (0.1 mmol, 1.0 eq.), **2a** (x eq.), 3DPAFIPN (0.005 mmol, 5 mol%), K_3PO_4 (1.0 eq.), TMEDA (3.0 eq.), DMA (1.0 mL), 5 Å MS (50.0 mg), CO_2 (1 atm), 455 nm 15W blue LEDs, –10 °C, 12 h. [b]Yields were determined by ^{1}H NMR with CH_2Br_2 (7 μL, 0.1 mmol) as an internal standard.

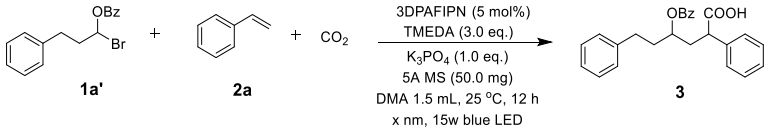


Table S11. Exploration of wavelength λ (nm) [a]

Entry	Light (nm)	Yield of **3** (%)
1	425 nm	70
2	440 nm	74
3	455 nm	80
4	470 nm	78
5	490 nm	78

[a]Reaction conditions: **1a'** (0.1 mmol, 1.0 eq.), **2a** (0.3 mmol, 3.0 eq.), 3DPAFIPN (0.005 mmol, 5 mol%), K_3PO_4 (1.0 eq.), TMEDA (3.0 eq.), DMA (1.0 mL), 5 Å MS (50.0 mg), CO_2 (1 atm), x nm 15W blue LEDs, –10 °C, 12 h. [b]Yields were determined by ^{1}H NMR with CH_2Br_2 (7 μL, 0.1 mmol) as an internal standard.

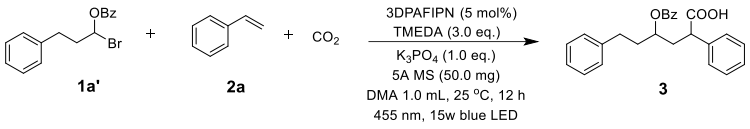


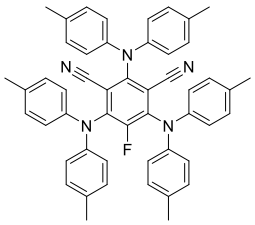
Table S12. The Charged temperature of CO_2

Entry	Charged temperature of CO_2 (°C)	Yield of **3** (%)
1	–10	80
2	–78	84

[a]Reaction conditions: **1a'** (1.0 eq.), **2a** (3.0 eq.), 3DPAFIPN (0.005 mmol, 5 mol%), K_3PO_4 (1.0 eq.), TMEDA (3.0 eq.), DMA (1.0 mL), 5 Å MS (50.0 mg), CO_2 (1 atm, charged at –78 °C), 455 nm 15W blue LEDs, –10 °C, 12 h. [b]Yields were determined by ^{1}H NMR with CH_2Br_2 (7 μL, 0.1 mmol) as an internal standard.

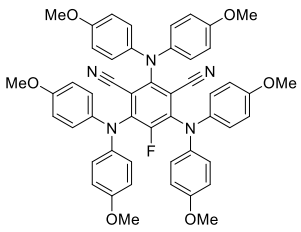
3. Preparation of Photocatalyst

2,4,6-Tris(di-p-tolylamino)-5-fluoroisophthalonitrile (3DPAFIPN-Me) [1]



To a solution of bis(4-methylphenyl)amine (5.0 mmol, 986.2 mg) in THF (20.0 mL), NaH (600.0 mg, 60% in mineral oil, 15.0 mmol) was added at 0 °C. The reaction mixture was stirred at 50 ℃ for 30 minutes. Finally, the reaction mixture was cooled to room temperature and tetrafluoroisophthalonitrile (200.0 mg, 1.0 mmol) was added. The resulting mixture was stirred at room temperature for 24 h. After the reaction was complete, 5.0 mL of water was carefully added dropwise to quench the excess NaH. After removal of THF, the residue was dissolved in DCM and washed with water. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (with PE: EA = 20: 1 to PE: DCM = 1: 1) to provide the 3DPAFIPN-Me as a yellow solid (504.4 mg, 69% yield): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.04 (d, *J* = 7.8 Hz, 12H), 6.86 (d, *J* = 7.6 Hz, 12H), 2.28 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.14 (d, *J* = 2.5 Hz), 143.54, 143.29, 143.18 (d, *J* = 11.0 Hz), 134.04, 133.32, 130.05, 129.99, 122.78, 122.73, 113.17 (d, *J* = 3.1 Hz), 108.11 (d, *J* = 3.2 Hz), 21.00. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -122.27. HRMS m/z (ESI) calculated for $C_{50}H_{42}FN_5$ $(M+H)^+$ 732.3497, found 732.3495.

2,4,6-Tris(bis(4-methoxyphenyl)amino)-5-fluoroisophthalonitrile (3DPAFIPN-OMe) [1]



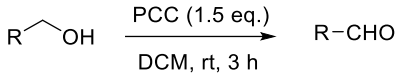
To a solution of 4,4'-Dimethoxydiphenylamine (5.0 mmol, 1.15 g) in THF (20.0 mL), NaH (600.0 mg, 60% in mineral oil, 15.0 mmol) was added at 0 °C. The reaction mixture was stirred at 50 ℃ for 30 minutes. Finally, the reaction mixture was cooled to room temperature and tetrafluoroisophthalonitrile (200.0 mg, 1.0 mmol) was added. The resulting mixture was stirred at room temperature for 24 h. After the reaction was complete, 5.0 mL of water was carefully added dropwise to quench the excess NaH. After removal of THF, the residue was dissolved in DCM and washed with water. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (with PE: EA = 10: 1 to EA: DCM = 20: 1) to provide the 3DPAFIPN-OMe as an orange solid (318.1

mg, 38% yield): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.89 (dd, *J* = 8.7, 5.8 Hz, 12H), 6.77 (dd, *J* = 8.9, 3.8 Hz, 12H), 3.76 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.51, 156.00, 139.76, 139.41, 124.28, 124.20, 114.72, 114.67, 55.54, 55.51. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -123.98. HRMS m/z (ESI) calculated for $C_{50}H_{42}FN_5O_6$ $(M+H)^+$ 828.3192, found 828.3192.

4. Preparation of starting materials

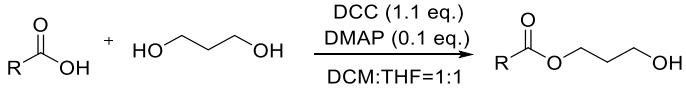
General procedure for the synthesis of the starting materials

Method A:[2]



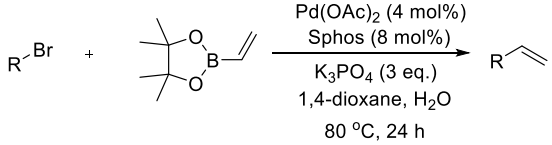
To a solution of alcohol (1.0 eq.) in DCM (0.2 M), PCC (pyridinium chlorochromate, 1.5 eq.) was added and the mixture was stirred at room temperature for 3 h. After the reaction was finished, the mixture was filtered through a pad of silica gel and washed with EA. The filtrate was concentrated under reduced pressure and the resulting crude product was purified by flash column chromatography to give the corresponding aldehyde.

Method B:[3]



To a cold (0 ℃) solution of acid (5.0 mmol, 1.0 eq.) and glycol (30.0 mmol, 6.0 eq.) in CH_2Cl_2-THF (1:1, V:V, 34.0 mL), DCC (*N*,*N*'-Dicyclohexylcarbodiimide, 5.5 mmol, 1.1 eq.) and DMAP (4-dimethylaminopyridine, 0.5 mmol, 0.1eq.) were added. The reaction mixture was stirred for 1 h at 0 ℃ and another 12 h at room temperature. After the reaction was complete, the suspension was filtered through a pad of celite, the precipitate was washed with EA. The filtrate was concentrated under reduced pressure and the resulting crude product was purified by flash column chromatography to give the corresponding alcohol.

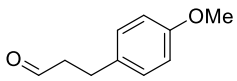
Method C:[4]



An oven-dried 25 mL Schlenk tube was charged with aryl bromide (1.0 eq.), $Pd(OAc)_2$ (4 mol%), SPhos (2-Dicyclohexylphosphino-2',6'-dimethoxybiphenyl, 8 mol%),

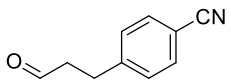
K_3PO_4 (3.0 eq.) under N_2 atmosphere. To the mixture was added vinyl boronic acid pinacol ester (2.0 eq.), 1,4-dioxane (0.25 M), H_2O (5.0 eq.) and the resulting mixture was stirred at 80 °C for 24 h. After the reaction was complete, the reaction mixture was diluted with EA and filtered through a pad of celite. The filtrate was concentrated under reduced pressure and the resulting crude product was purified by flash column chromatography to give the corresponding alkene.

3-(4-Methoxyphenyl)propanal (1b)



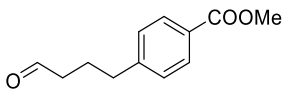
According to Method A, the reaction was carried out with corresponding alcohol (496 μL, 3.0 mmol), PCC (970.1 mg, 4.5 mmol) in CH_2Cl_2 (15.0 mL). The crude material was purified by flash column chromatography on silica gel (PE: EA = 50: 1) to provide the title compound as a colorless oil (443.0 mg, 90% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.81 (s, 1H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 2.91 (t, *J* = 7.5 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 2H). All data are in accordance with the literature.[5]

4-(3-Oxopropyl)benzonitrile (1e)



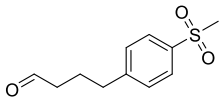
According to Method A, the reaction was carried out with corresponding alcohol (296 μL, 2.0 mmol), PCC (646.7 mg, 3.0 mmol) in CH_2Cl_2 (10.0 mL). The crude material was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to provide the title compound as a white solid (264.1 mg, 83% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.82 (s, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.01 (t, *J* = 7.4 Hz, 2H), 2.82 (t, *J* = 7.4 Hz, 2H). All data are in accordance with the literature.[6]

Methyl 4-(4-oxobutyl)benzoate (1f)



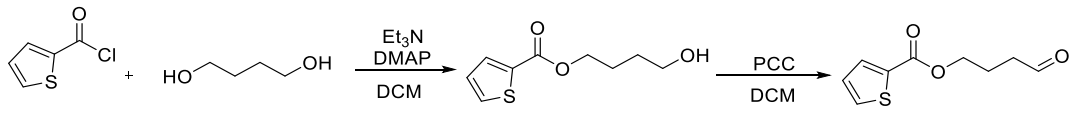
According to Method A, the reaction was carried out with corresponding alcohol (416.5 mg, 2.0 mmol), PCC (646.7 mg, 3.0 mmol) in CH_2Cl_2 (10.0 mL). The crude material was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to provide the title compound as a white solid (362.7 mg, 88 % yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.77 (t, *J* = 1.5 Hz, 1H), 7.96 (dt, *J* = 8.0, 1.9 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 3.90 (s, 3H), 2.71 (t, *J* = 7.5 Hz, 2H), 2.46 (td, *J* = 7.3, 1.5 Hz, 2H), 2.01 – 1.95 (m, 2H). All data are in accordance with the literature.[7]

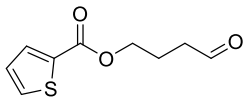
4-(4-(Methylsulfonyl)phenyl)butanal (1g) [8]



In glovebox, an oven-dried 25 mL Schlenk tube was charged with the 1-bromo-4-(methylsulfonyl)benzene (705.3 mg, 3.0 mmol, 1.0 eq.), anhydrous LiOAc (217.8 mg, 3.3 mmol, 1.1 eq.), LiCl (381.5 mg, 9.0 mmol, 3 eq.), TBAB (483.6 mg, 1.5 mmol, 0.5 eq.) and DMF (10.0 mL). To the mixture was added 3-buten-1-ol (310 μL, 3.6 mmol, 1.2 eq.) and $Pd(OAc)_2$ (16.8 mg, 0.075 mmol, 2.5 mol %) and the resulting mixture was stirred at 80 °C for 24 h. After the reaction was complete, the reaction mixture was filtered through a pad of celite, the precipitate was washed with EA. The filtrate was concentrated under reduced pressure and the resulting crude product was purified by flash column chromatography on silica gel to give the **1g** as a white solid (210.2 mg, 31% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.79 (t, *J* = 1.4 Hz, 1H), 7.88 – 7.85 (m, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 3.04 (s, 3H), 2.75(t, *J* = 7.8 Hz, 2H), 2.50 (td, *J* = 7.2, 1.4 Hz, 2H), 2.04 – 1.95(m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 201.64, 148.06, 138.60, 129.52, 127.78, 44.70, 43.06, 35.02, 23.32. HRMS m/z (ESI) calculated for $C_{11}H_{14}O_3S$ $(M+H)^+$ 227.0736, found 227.0736.

4-Oxobutyl thiophene-2-carboxylate (1h)

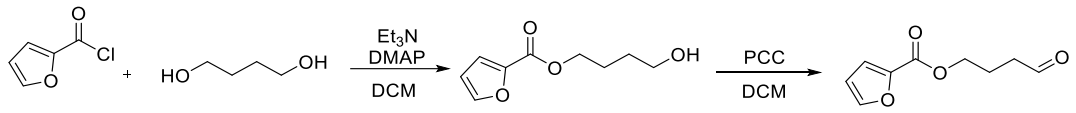


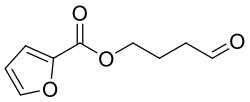


To a solution of 1,4-butanediol (2.66 mL, 30.0 mmol, 3.0 eq.), Et_3N (1.95 mL, 14.0 mmol, 1.4 eq.), and DMAP (122.2 mg, 1.0 mmol, 0.1 eq.) in DCM (20.0 mL), 2-thiophenecarbonyl chloride (1.07 mL, 10.0 mmol, 1.0 eq.) was added at 0 °C. The mixture was stirred until the reaction was completed (monitored by TLC). The reaction was quenched with saturated aqueous NH_4Cl solution. Then the aqueous layer was extracted with DCM (3 × 20 mL), the combined organic layers were washed with brine, and dried over anhydrous Na_2SO_4. The solvents were evaporated under reduced pressure, and the crude alcohol was used in the next step without further purification. According to Method A, the reaction was carried out with corresponding alcohol (416.5 mg, 2.0 mmol, 1.0 eq.), PCC (646.7 mg, 3.0 mmol, 1.5 eq.) in CH_2Cl_2 (10.0 mL). The crude material was purified by flash column chromatography on silica gel (PE: EA = 10: 1) to provide the title compound as a colorless oil (209.9 mg, 53% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.82 (s, 1H), 7.78 (d, *J* = 4.0 Hz, 1H), 7.56 (d, *J* = 5.0 Hz, 1H), 7.09 (t, *J* = 4.5 Hz, 1H), 4.33 (t, *J* =

6.5 Hz, 2H), 2.61(t, *J* = 7.3 Hz, 2H), 2.12 – 2.06 (m, 2H). All data are in accordance with the literature.[9]

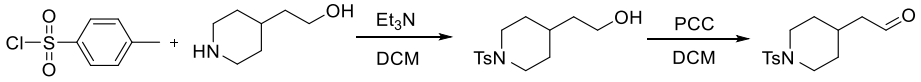
4-Oxobutyl furan-2-carboxylate (1i)

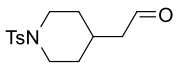




To a solution of 1,4-butanediol (2.66 mL, 30.0 mmol, 3.0 eq.), Et_3N (1.95 mL, 14.0 mmol, 1.40 eq.), and DMAP (122.2 g, 1.0 mmol, 0.1 eq.) in DCM (20.0 mL), 2-Furoyl chloride (986 μL,10.0 mmol, 1.0 eq.) was added at 0 °C. The mixture was stirred until the reaction was completed (monitored by TLC). The reaction was quenched with saturated aqueous NH_4Cl solution. Then the aqueous layer was extracted with DCM (3 × 20 mL), the combined organic layers were washed with brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude alcohol was used in the next step without further purification. According to Method A, the reaction was carried out with corresponding alcohol (368.1 mg, 2.0 mmol, 1.0 eq.), PCC (646.7 mg, 3.0 mmol, 1.5 eq.) in CH_2Cl_2 (10.0 mL). The crude material was purified by flash column chromatography on silica gel (PE: EA = 10: 1) to provide the title compound as a colorless oil (167.5 mg, 46% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.81 (s, 1H), 7.57 (s, 1H), 7.16 (d, *J* = 3.5 Hz, 1H), 6.51 – 6.50 (m, 1H), 4.33 (t, *J* = 6.5 Hz, 2H), 2.61 (t, *J* = 7.3 Hz, 2H), 2.12 – 2.06 (m, 2H). All data are in accordance with the literature.[9]

2-(1-Tosylpiperidin-4-yl)acetaldehyde (1j)

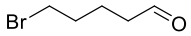




The TsCl (783 μL, 5.5 mmol, 1.1 eq.) was added to a solution of 4-piperidineethanol (688 μL, 5.0 mmol, 1.0 eq.) and 1.25 mL Et_3N in 10.0 mL anhydrous DCM at 0 °C, the mixture was stirred at room temperature for 2 h. After the reaction was complete, the reaction mixture was diluted with DCM and washed with 1 M HCl, saturated solution of $NaHCO_3$ and brine. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the

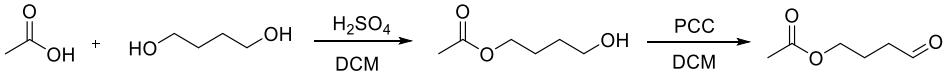
corresponding alcohol. According to Method A, the reaction was carried out with corresponding alcohol (567.0 mg, 2.0 mmol), PCC (646.7 mg, 3.0 mmol) in CH_2Cl_2 (10.0 mL). The crude material was purified by flash column chromatography on silica gel (PE: EA = 5: 1) to provide the title compound as a white solid (320.5 mg, 57% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.72 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.75 (d, *J* = 12.0 Hz, 2H), 2.43 (s, 3H), 2.37 (d, *J* = 6.5 Hz, 2H), 2.27 (td, *J* = 12.0, 3.8 Hz, 2H), 1.86 – 1.79 (m, 1H), 1.75 (d, *J* = 12.0 Hz, 2H), 1.36 (qd, *J* = 9.3, 4.0 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 201.10, 143.66, 133.12, 129.75, 127.83, 49.97, 46.30, 31.36, 29.76, 21.64. HRMS m/z (ESI) calculated for $C_{14}H_{19}NO_3S$ $(M+H)^+$ 282.1158, found 282.1158.

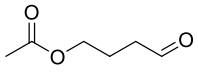
5-Bromopentanal (1n)



According to Method A, the reaction was carried out with corresponding alcohol (242 μL, 2.0 mmol), PCC (646.7 mg, 3.0 mmol) in CH_2Cl_2 (10.0 mL). The crude material was purified by flash column chromatography on silica gel (PE: EA = 50: 1) to provide the title compound as a colorless oil (265.6 mg, 81% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.77 (s, 1H), 3.41 (t, *J* = 6.5 Hz, 2H), 2.48 (t, *J* = 7.3 Hz, 2H), 1.92 – 1.86 (m, 2H), 1.81 – 1.76 (m, 2H). All data are in accordance with the literature.[10]

4-Oxobutyl acetate (1o)

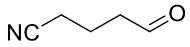




To a solution of 1,4-butanediol (0.88 mL, 10.0 mmol, 1.0 eq.) in DCM (20.0 mL), AcOH (561 μL, 9.8 mmol, 0.98 eq.) and H_2SO_4 (30 μL, 0.5 mmol, 0.05 eq.) were added at 0 °C. After stirring for 1 h at room temperature, the solution was treated with water and extracted with DCM. The organic phase was washed with a saturated solution of Na_2CO_3 and brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the corresponding alcohol which was used in the next step without further purification. According to Method A, the reaction was carried out with corresponding alcohol (264.2 mg, 2.0 mmol), PCC (646.7 mg, 3.0 mmol) in CH_2Cl_2 (10.0 mL). The crude material was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to provide the title compound as a colorless oil (184.7 mg, 71% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.80 (t, *J* = 1.3 Hz,

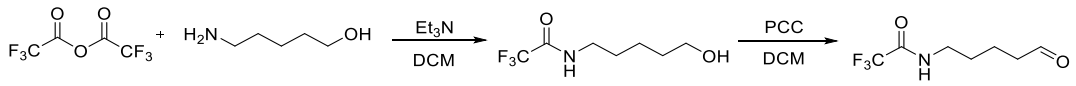
1H), 4.10 (td, *J* = 6.5, 2.0 Hz, 2H), 2.55 (td, *J* = 7.3, 1.5 Hz, 2H), 2.05 (t, *J* = 2.3 Hz, 3H), 2.01 – 1.95 (m, 2H). All data are in accordance with the literature.[11]

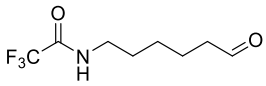
5-Oxopentanenitrile (1p)



According to Method A, the reaction was carried out with corresponding alcohol (102 μL, 1.0 mmol), PCC (323.9 mg, 1.5 mmol) in CH_2Cl_2 (5.0 mL). The crude material was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to provide the title compound as a colorless oil (80.6 mg, 83 % yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.80 (s, 1H), 2.68 (t, *J* = 6.8 Hz, 2H), 2.44 (t, *J* = 7.0 Hz, 2H), 2.00 – 1.94 (m, 2H). All data are in accordance with the literature.[12]

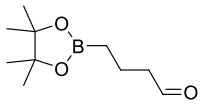
2,2,2-Trifluoro-*N*-(5-oxopentyl)acetamide (1q)





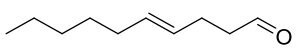
An oven-dried 100 mL flask was charged with 5-aminopentan-1-ol (1.03 g, 10.0 mmol, 1.0 eq.), triethylamine (1.52 g, 15 mmol, 1.5 eq.) and dry DCM (20.0 mL). To the mixture was added trifluoroacetic anhydride (2.73 g, 13.0 mmol, 1.3 eq.) dropwise at 0 °C and the resulting mixture was stirred at room temperature for 12 h. The reaction mixture was quenched with saturated NH_4Cl solution and extracted with DCM. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel (PE: EA = 2: 1) to provide the corresponding alcohol as a yellow oil (1.83 g, 86% yield). According to Method A, the reaction was carried out with corresponding alcohol (426.2 mg, 2.0 mmol), PCC (646.7 mg, 3.0 mmol) in CH_2Cl_2 (10.0 mL). The crude material was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to provide the title compound as a yellow oil (346.2 mg, 82% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.73 (t, *J* = 1.6 Hz, 1H), 6.90 (s, 1H), 3.34 (q, *J* = 6.8 Hz, 2H), 2.44 (td, *J* = 7.2, 1.6 Hz, 2H), 1.67 – 1.55 (m, 4H), 1.39 – 1.31 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 202.75, 157.49 (q, *J* = 36.7 Hz), 115.98 (q, *J* = 290.5 Hz), 43.65, 39.70, 28.64, 26.13, 21.41. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -76.00. HRMS m/z (ESI) calculated for $C_8H_{12}F_3NO_2$ $(M+H)^+$ 212.0893, found 212.0895.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)butanal (1r) [13]



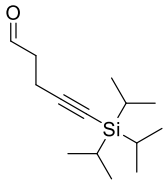
To a solution of ethyl 4-(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolan-2-yl)butanoate (494 μL, 2.0 mmol, 1.0 eq.) in DCM (15.0 mL), DIBAL-H (1.47 mL, 1.5 M in hexane, 1.1 eq.) was added at −78 °C under N_2 atmosphere. After stirring for 1 h at –78 °C, the reaction mixture was quenched with MeOH and saturated NH_4Cl and extracted with DCM. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel (PE: EA = 10: 1) to provide the title compound as a colorless oil (198.1 mg, 53% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.75 (t, *J* = 2.0 Hz, 1H), 2.43 (td, *J* = 7.3, 2.8 Hz, 2H), 1.79 – 1.73 (m, 2H), 1.24 (s, 12H), 0.83 (t, *J* = 8.0 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 203.18, 83.29, 46.21, 24.97, 16.99. HRMS m/z (ESI) calculated for $C_{10}H_{19}BO_3$ $(M+H)^+$ 199.1500, found 199.1500.

(*E*)-Dec-4-enal (1s)



According to Method A, the reaction was carried out with corresponding alcohol (312.5 mg, 2.0 mmol), PCC (646.7 mg, 3.0 mmol) in CH_2Cl_2 (10.0 mL). The crude material was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to provide the title compound as a colorless oil (265.1 mg, 86% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.77 (s, 1H), 5.46 – 5.41 (m, 1H), 5.35 – 5.30 (m, 1H), 2.48 (t, *J* = 7.5 Hz, 2H), 2.39 – 2.35 (m, 2H), 2.06 – 2.01 (m, 2H), 1.36 – 1.27 (m, 6H), 0.89 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 202.45, 131.90, 127.15, 43.99, 31.63, 29.39, 27.32, 22.69, 20.22, 14.19. HRMS m/z (ESI) calculated for $C_{10}H_{18}O$ $(M+H)^+$ 155.1430, found 155.1426.

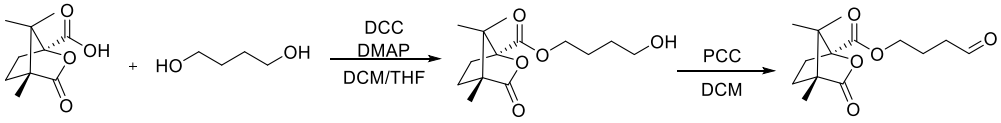
5-(Triisopropylsilyl)pent-4-ynal (1t)

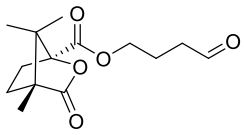


A mixture of $Pd(OAc)_2$ (56.1 mg, 0.25 mmol, 10 mol %) and 0.75 mL of PMe_3 solution (0.75 mmol, 1.0 M PMe_3 dissolved in toluene, 30 mol%) was stirred at 110 °C under N_2 for 10 min until all $Pd(OAc)_2$ was dissolved. Then 2.5 mL water and 5.0 mL acetone were added, followed by a mixture of terminal alkyne (620 μL, 2.5 mmol, 1.0 eq.) and acrolein (834 μL, 12.5 mmol, 5.0 eq.). After stirring for 7 h at 60 °C, the reaction mixture was extracted with ethyl ether, the combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel (PE: EA = 20: 1 to PE: DCM = 5: 1) to provide the title compound as a colorless oil (303.7 mg, 51% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ

9.81 (t, *J* = 1.4 Hz, 1H), 2.69 – 2.65 (m, 2H), 2.59 – 2.56 (m, 2H), 1.07 – 0.99 (m, 21H). All data are in accordance with the literature.[14]

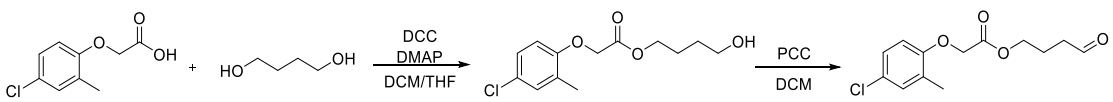
4-Oxobutyl(1S,4R)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxy late (1aa)

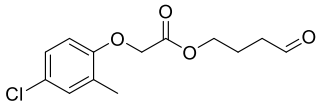




According to Method B, the reaction was carried out with the (1*S*)-(-)-camphanic acid (991.1 mg, 5.0 mmol), glycol (2.66 mL, 30.0 mmol,), DCC (1.134 g, 5.5 mmol), DMAP (61.1 mg, 0.5 mmol,) and CH_2Cl_2/THF (34.0 mL). The crude product was purified by flash column chromatography on silica gel (PE: EA = 2: 1) to afford corresponding alcohol as a colorless oil (783.4 mg, 58% yield). According to Method A, the reaction was carried out with corresponding alcohol (540.3 mg, 2.0 mmol), PCC (646.7 mg, 3.0 mmol) in CH_2Cl_2 (10.0 mL). The crude material was purified by flash column chromatography on silica gel (PE: EA = 10: 1) to provide the title compound as a colorless oil (439.7 mg, 82% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.75 (s, 1H), 4.21 (t, *J* = 6.4 Hz, 2H), 2.54 (t, *J* = 7.1 Hz, 2H), 2.40 – 2.33 (m, 1H), 2.02 – 1.85 (m, 4H), 1.63 (ddd, *J* = 13.4, 9.2, 4.2 Hz, 1H), 1.06 (s, 3H), 1.00 (s, 3H), 0.90 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 200.84, 178.10, 167.41, 91.06, 64.53, 54.76, 54.16, 40.18, 30.65, 28.91, 21.17, 16.76, 16.74, 9.69. HRMS m/z (ESI) calculated for $C_{14}H_{20}O_5$ $(M+H)^+$ 269.1384, found 269.1388.

4-Oxobutyl 2-(4-chloro-2-methylphenoxy)acetate (1ab)

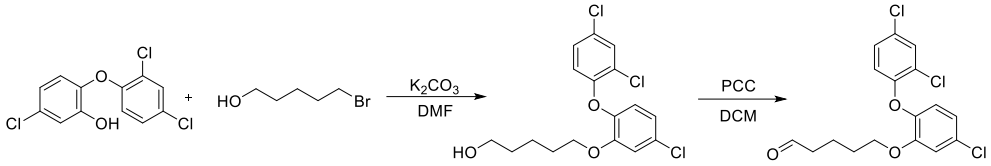


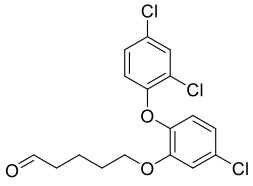


According to Method B, the reaction was carried out with the 2-(4-chloro-2-methylphenoxy)acetic acid (1.00 g, 5.0 mmol), glycol (2.66 mL, 30.0 mmol), DCC (1.13 g, 5.5 mmol), DMAP (61.1 mg, 0.5 mmol) and CH_2Cl_2/THF (34 mL). The crude product was purified by flash column chromatography on silica gel (PE: EA = 5: 1) to afford

corresponding alcohol as white solid (1.10 g, 81% yield). According to Method A, the reaction was carried out with corresponding alcohol (544.2 mg, 2.0 mmol), PCC (646.7 mg, 3.0 mmol) in CH_2Cl_2 (10.0 mL). The crude material was purified by flash column chromatography on silica gel (PE: EA = 10: 1) to provide the title compound as a colorless oil (448.3 mg, 83% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.75 (s, 1H), 7.14 (d, *J* = 2.7 Hz, 1H), 7.08 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.61 (d, *J* = 8.6 Hz, 1H), 4.62 (s, 2H), 4.23 (t, *J* = 6.3 Hz, 2H), 2.49 (t, *J* = 7.1 Hz, 2H), 2.25 (s, 3H), 1.99 (p, *J* = 6.7 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 200.97, 168.83, 154.71, 130.90, 129.33, 126.40, 126.29, 112.27, 65.73, 64.33, 40.27, 21.20, 16.17. HRMS m/z (ESI) calculated for $C_{13}H_{15}ClO_4$ $(M+H)^+$ 271.0732, found 271.0729.

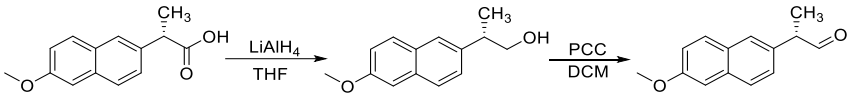
5-(5-Chloro-2-(2,4-dichlorophenoxy)phenoxy)pentanal (1ac)

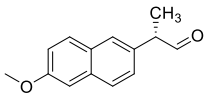




An oven-dried 50 mL flask was charged with triclosan (2.90 g, 10.0 mmol, 2.0 eq.), potassium carbonate (1.38 g, 10.0 mmol, 2.0 eq.), 5-bromopentan-1-ol (605 μL, 5.0 mmol, 1.0 eq.) and DMF (10.0 mL). After stirring for 1 h at 80 °C, the reaction mixture was diluted with water and extracted with EA. The combined organic layers were washed with NaOH (aq, 2 M, 10.0 mL) and saturated aqueous $NaHCO_3$ (15.0 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (PE: EA = 2: 1) to afford the corresponding alcohol as a white solid (1.41 g, 76% yield). According to Method A, the reaction was carried out with corresponding alcohol (748.0 mg, 2.0 mmol), PCC (646.7 mg, 3.0 mmol) in CH_2Cl_2 (10.0 mL). The crude material was purified by flash column chromatography on silica gel (PE: EA = 15: 1) to provide the title compound as a colorless oil (580.3 mg, 78% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.69 (t, *J* = 1.6 Hz, 1H), 7.43 (d, *J* = 2.5 Hz, 1H), 7.08 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.98 – 6.92 (m, 3H), 6.63 (d, *J* = 8.8 Hz, 1H), 3.93 (t, *J* = 5.9 Hz, 2H), 2.38 (td, *J* = 7.2, 1.6 Hz, 2H), 1.70 – 1.65 (m, 2H), 1.59 – 1.53 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 202.13, 152.72, 150.94, 142.99, 130.85, 130.26, 127.91, 127.73, 124.38, 122.43, 121.26, 117.79, 114.84, 68.75, 43.40, 28.41, 18.67. HRMS m/z (ESI) calculated for $C_{17}H_{15}Cl_3O_3$ $(M+Na)^+$ 394.9979, found 394.9986.

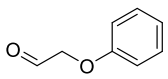
(*S*)-2-(6-Methoxynaphthalen-2-yl)propanal (1ad)





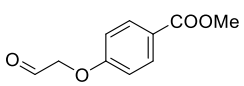
To a solution of (*S*)-naproxen (1.15 g, 5.0 mmol, 1.0 eq.) in THF (15.0 mL), $LiAlH_4$ (380.0 mg, 10.0 mmol, dissolved in 10.0 mL THF) was slowly added at 0 ^oC under N_2 atmosphere. After stirring for 2 h at room temperature, the mixture was quenched by water and filtered through a pad of silica gel. The filtrate was evaporated under reduced pressure and the crude alcohol was used in the next step without further purification. According to Method A, the reaction was carried out with corresponding alcohol (432.2 mg, 2.0 mmol), PCC (646.7 mg, 3.0 mmol) in CH_2Cl_2 (10.0 mL). The crude material was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to provide the title compound as a colorless oil (252.6 mg, 59% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.75 (s, 1H), 7.76 – 7.71 (m, 2H), 7.60 (s, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.17 (d, *J* = 8.5 Hz, 1H), 7.14 (s, 1H), 3.93 (s, 3H), 3.79 – 3.75 (m, 1H), 1.52 (d, *J* = 6.0 Hz, 3H). All data are in accordance with the literature.[15]

2-Phenoxyacetaldehyde (1ae) [16]



To a solution of phenoxyethanol (624 μL, 5.0 mmol, 1.0 eq.) in EA (75.0 mL), IBX (2-Iodoxybenzoic acid, 2.80 g, 10.0 mmol, 2.0 eq.) was added. After refluxing for 6 h, the mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure and the resulting crude product was purified by flash column chromatography on silica gel (PE: EA = 10: 1) to provide the title compound as a colorless oil (551.0 mg, 81% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.87 (s, 1H), 7.34 – 7.30 (m, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 2H), 4.58 (d, *J* = 1.1 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 199.63, 157.76, 128.79, 122.12, 114.70, 72.77. HRMS m/z (ESI) calculated for $C_8H_8O_2$ $(M+H)^+$ 137.0597, found 137.0595.

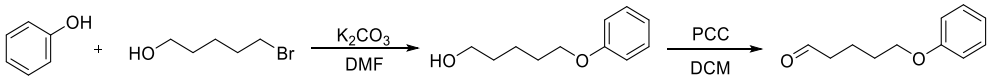
Methyl 4-(2-oxoethoxy)benzoate (1af) [16]

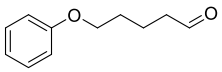


To a solution of methyl 4-(2-hydroxyethoxy)benzoate (392.0 mg, 2.0 mmol, 1.0 eq.) in EA (30.0 mL), IBX (1.12 g, 4.0 mmol, 2.0

eq.) was added. After refluxing for 6 h, the mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure and the resulting crude product was purified by flash column chromatography on silica gel (PE: EA = 3: 1) to provide the title compound as a white solid (197.9 mg, 51% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.85 (s, 1H), 8.01 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 4.63 (s, 2H), 3.88 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 198.22, 166.65, 161.27, 131.93, 124.05, 114.30, 72.62, 52.12. HRMS m/z (ESI) calculated for $C_{10}H_{10}O_4$ $(M+H)^+$ 195.0652, found 195.0646.

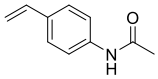
5-Phenoxypentanal (1ag)





An oven-dried 50 mL flask was charged with phenol (941.1 mg, 10.0 mmol, 2.0 eq.), potassium carbonate (1.38 g, 10.0 mmol, 2.0 eq.), 5-bromopentan-1-ol (605 μL, 5.0 mmol, 1.0 eq.) and DMF (10.0 mL). After stirring for 12 h at 80 °C, the reaction mixture was diluted with water and extracted with EA. The combined organic layers were washed with aqueous NaOH (2 M, 10.0 mL), saturated aqueous $NaHCO_3$ (15.0 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel (PE: EA = 5: 1) to provide the corresponding alcohol as a white solid (1.59 g, 88% yield). According to Method A, the reaction was carried out with corresponding alcohol (360.2 mg, 2.0 mmol), PCC (646.7 mg, 3.0 mmol) in CH_2Cl_2 (10.0 mL). The crude material was purified by flash column chromatography on silica gel (PE: EA = 15: 1) to provide the title compound as a white solid (324.1 mg, 91% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.80 (t, *J* = 1.7 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 2H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 2H), 3.99 – 3.97 (m, 2H), 2.55 – 2.52 (m, 2H), 1.84 – 1.83 (m, 4H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 202.41, 158.99, 129.57, 120.81, 114.57, 67.32, 43.61, 28.79, 18.98. HRMS m/z (ESI) calculated for $C_{11}H_{14}O_2$ $(M+H)^+$ 179.1067, found 179.1068.

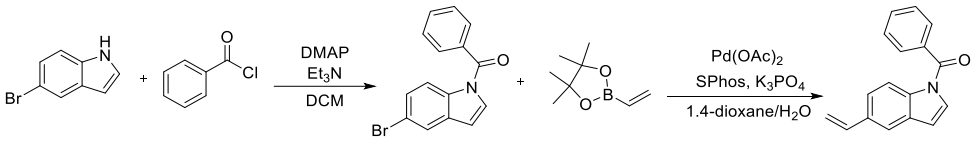
***N*-(4-Vinylphenyl)acetamide (2i)**

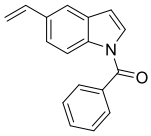


To a solution of 4-vinylaniline (357.5 mg, 3.0 mmol, 1.0 eq.) in DCM (7.5 mL), acetic anhydride (0.4 mL, 3.6 mmol, 1.2 eq.) was added under

N_2 atmosphere. After stirring for 5 h at room temperature, the reaction mixture was washed with a saturated solution of Na_2CO_3, dried over $MgSO_4$ and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel (PE: EA = 2: 1) to provide the title compound as a white solid (439.8 mg, 91% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** 7.47 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 6.66 (q, *J* = 9.5 Hz, 1H), 5.67 (d, *J* = 17.6 Hz, 1H), 5.19 (d, *J* = 11.2 Hz, 1H), δ 2.17 (s, 3H). All data are in accordance with the literature.[17]

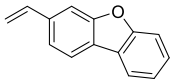
Phenyl(5-vinyl-1*H*-indol-1-yl)methanone (2q)





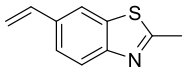
An oven-dried 100 mL flask was charged with 5-Bromoindole (1.96 g, 10.0 mmol, 1.0 eq.), DMAP (122.2 mg, 1.0 mmol, 0.1 eq.), triethylamine (2.08 mL, 15.0 mmol, 1.5 eq.) in DCM (20.0 mL). To the mixture was added benzoyl chloride (1.39 mL, 12.0 mmol, 1.2 eq.) dropwise at 0 °C. After stirring for 12 h at room temperature, the reaction mixture was quenched with 1.0 M HCl. The mixture was extracted with DCM, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel (PE: EA = 4: 1) to provide the (5-bromo-1*H*-indol-1-yl)(phenyl)methanone as a white solid (2.03 g, 68% yield). According to Method C, the reaction was carried out with (5-bromo-1*H*-indol-1-yl)(phenyl)methanone (1.49 g, 5.0 mmol), $Pd(OAc)_2$ (44.9 mg, 0.2 mmol), SPhos (164.2 mg, 0.4 mmol), K_3PO_4 (3.18 g, 15.0 mmol), pinacol vinylboronate (1.7 mL, 10.0 mmol), 1,4-dioxane (15.0 mL) and H_2O (450 μL). The crude material was purified by flash column chromatography on silica gel (PE: EA = 5: 1) to provide the title compound as a white solid (877.2 mg, 71% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** 8.36 – 8.32 (m, 1H), 7.76 – 7.73 (m, 2H), 7.63 – 7.59 (m, 2H), 7.55 – 7.47 (m, 3H), 7.29 (d, *J* = 4.5 Hz, 1H), 6.84 (ddd, *J* = 17.6, 10.9, 2.0 Hz, 1H), 6.60 (dd, *J* = 3.8, 0.7 Hz, 1H), 5.82 – 5.77 (m, 1H), 5.27 (d, *J* = 11.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.67, 137.15, 135.82, 134.60, 133.82, 132.05, 131.22, 129.29, 128.72, 128.22, 123.29, 118.84, 116.48, 113.22, 108.81. HRMS m/z (ESI) calculated for $C_{17}H_{13}NO$ $(M+H)^+$ 248.1070, found 248.1068.

3-Vinyldibenzo[*b*,*d*]furan (2r)



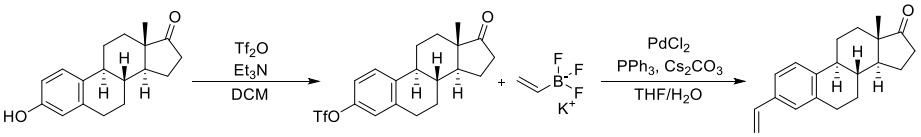
According to Method C, the reaction was carried out with 3-bromodibenzofuran (741.3 mg, 3.0 mmol), $Pd(OAc)_2$ (26.9 mg, 0.12 mmol), SPhos (98.5 mg, 0.24 mmol), K_3PO_4 (1.91 g, 9.0 mmol), vinyl boronic acid pinacol ester (1.02 mL, 6.0 mmol), 1,4-dioxane (9.0 mL) and H_2O (270 μL). The crude material was purified by flash column chromatography on silica gel (PE: EA = 10: 1) to provide the title compound as a white solid (413.4 mg, 71% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** 7.90 (dd, *J* = 21.8, 7.8 Hz, 2H), 7.61 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 5.86 (d, *J* = 17.5 Hz, 1H), 5.33 (d, *J* = 11.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.83, 156.81, 137.34, 136.99, 127.25, 124.25, 124.04, 122.92, 121.53, 120.74, 120.65, 114.46, 111.80, 109.16. HRMS m/z (ESI) calculated for $C_{14}H_{10}O$ $(M+H)^+$ 195.0804, found 195.0801.

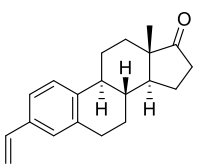
2-Methyl-6-vinylbenzo[*d*]thiazole (2t)



According to Method C, the reaction was carried out with 3-bromodibenzofuran (494.2 mg, 2.0 mmol, 1.0 eq.), $Pd(OAc)_2$ (18.0 mg, 0.08 mmol), SPhos (65.7 mg, 0.16 mmol), K_3PO_4 (1.27 g, 6.0 mmol), vinyl boronic acid pinacol ester (0.68 mL, 4.0 mmol), 1,4-dioxane (6.0 mL) and H_2O (180 μL). The crude material was purified by flash column chromatography on silica gel (PE: EA = 2: 1) to provide the title compound as a white solid (290.6 mg, 83% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.88 (d, *J* = 10.1 Hz, 1H), 7.82 (s, 1H), 7.52 (d, *J* = 8.5 Hz, 1H), 6.80 (dd, *J* = 16.7, 10.1 Hz, 1H), 5.79 (d, *J* = 17.5 Hz, 1H), 5.30 (d, *J* = 10.9 Hz, 1H), 2.83 (s, 3H). All data are in accordance with the literature.[18]

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (2w)

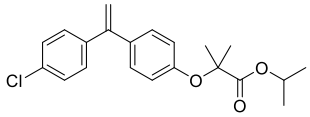




To a solution of estrone (1.35 g, 5.0 mmol, 1.0 eq.) in DCM (20.0 mL), Et_3N (1.4 mL, 10.0 mmol, 2.0 eq.) and Tf_2O (0.93 mL, 5.5 mmol, 1.1 eq.) were added at 0 °C. After stirring for 5 h at room temperature, the mixture was added a saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted with DCM, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column

chromatography on silica gel (PE: EA = 5: 1) to provide the estrone-triflate as a white solid (1.25 g, 62%). An oven-dried 100 mL Schlenk tube was charged with estrone-triflate (1.21 g, 3.0 mmol), potassium vinyl trifluoroborate (803.7 mg, 6.0 mmol, 2.0 eq.), $PdCl_2$ (53.2 mg, 0.3 mmol, 0.1 eq.), PPh_3 (94.4 mg, 0.36 mmol, 0.12 eq.) and Cs_2CO_3 (2.94 g, 9.0 mmol, 3.0 eq.). To the mixture was added THF (30.0 mL) and distilled water (4.0 mL) under N_2 atmosphere. After stirring for 15 h at 85 °C, the mixture was extracted with DCM, the combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel (PE: EA = 10: 1) to provide the title compound as a white solid (764.9 mg, 91% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.28 – 7.22 (m, 2H), 7.15 (s, 1H), 6.68 (q, *J* = 9.5 Hz, 1H), 5.71 (d, *J* = 17.5 Hz, 1H), 5.20 (d, *J* = 10.5 Hz, 1H), 2.93 (q, *J* = 4.5 Hz, 2H), 2.52 (q, *J* = 6.9 Hz, 1H), 2.46 – 2.42 (m, 1H), 2.31(td, *J* = 11.0, 4.0 Hz, 1H), 2.19 – 1.96 (m, 4H), 1.68 – 1.42 (m, 6H), 0.92 (s, 3H). All data are in accordance with the literature.[19]

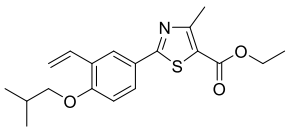
(2-(4-(1-(4-Chlorophenyl)vinyl)phenoxy)-2-methylpropanoyl) (isopropyl) oxonium (2x)



To a solution of methyltriphenylphosphonium bromide (1.07 g, 3.0 mmol, 1.5 eq.) in THF (20.0 mL), NaH (120.0 mg, 3.0 mmol, 1.5 eq., 60 % dispersed in mineral oil) was added at 0 °C under N_2 atmosphere, the mixture was stirred for 30 minutes at 0 °C. To the mixture was added fenofibrate (721.7 mg, 2.0 mmol, 1.0 eq. dissolved in 5.0 mL THF) at 0 °C and the resulting mixture was stirred at room temperature for 12 h. The reaction mixture was quenched with water in ice bath and extracted with EA. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (PE: EA = 10: 1) to provide the title compound as a white solid (479.9 mg, 67% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.76 – 7.72 (m, 4H), 7.49 (d, *J* = 7.8 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.78 (dd, *J* = 17.7, 10.9 Hz, 1H), 5.88 (d, *J* = 17.6 Hz, 1H), 5.39 (d, *J* = 10.8 Hz, 1H), 5.09 (dt, *J* = 12.4, 6.2 Hz, 1H), 1.66 (s, 6H), 1.20 (d, *J* = 6.2 Hz, 6H). All data are in accordance with the literature.[20]

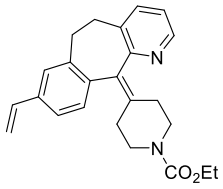
Ethyl 2-(4-isobutoxy-3-vinylphenyl)-4-methylthiazole-5-carboxylate (2y)

To a solution of methyltriphenylphosphonium bromide (1.07 g, 3.0 mmol, 1.5 eq.) in THF (10.0 mL), *n*-BuLi (0.88 mL, 1.1 eq., 2.5 M in hexanes) was added at 0 °C under



N_2 atmosphere, the mixture was stirred for 30 minutes at room temperature. To the mixture was added ethyl 2-(3-formyl-4-hydroxyphenyl)-4-methylthiazole-5-carboxylate (638.8 mg, 2.0 mmol, 1.5 eq.) at 0°C. After stirring for 12 h at room temperature, the mixture was poured into saturated aqueous NH_4Cl and extracted with EA. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (PE: EA = 2: 1) to provide the title compound as a yellow solid (524.6 mg, 76% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.05 (s, 1H), 7.82 (d, *J* = 10.6 Hz, 1H), 7.06 (dd, *J* = 17.8, 11.1 Hz, 1H), 6.89 (d, *J* = 8.6 Hz, 1H), 5.89 (d, *J* = 17.7 Hz, 1H), 5.35 (d, *J* = 12.0 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.81 (d, *J* = 6.3 Hz, 2H), 2.77 (s, 3H), 2.17 – 2.12 (m, 1H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.07 (d, *J* = 6.6 Hz, 6H). All data are in accordance with the literature.[21]

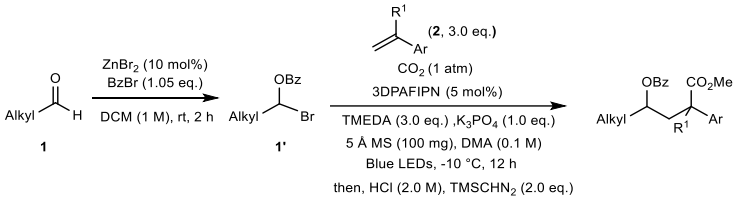
Ethyl-4-(8-vinyl-5,6-dihydro-11H-benzo[5,6]cyclohEpta[1,2-b]pyridin-11-ylidene) piperidine-1-carboxylate (2z)



An oven-dried 100 mL Schlenk tube was charged with loratadine (1.53 g, 4.0 mmol), $Pd(OAc)_2$ (44.9 mg, 0.2 mmol, 5 mol%), SPhos (164.2 mg, 0.4 mmol, 10 mol%), potassium vinyl trifluoroborate (803.7 mg, 6.0 mmol), K_2CO_3 (1.60 g, 12.0 mmol) and dioxane:H_2O (6:1,V:V, total 50.0 mL). After stirring for 18 h at 90 °C, the mixture was cooled to room temperature and filtered through a pad of celite. The organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel (PE: EA = 2: 1) to provide the title compound as a yellow solid (1.33 g, 89% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.39 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.43 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.24 – 7.20 (m, 2H), 7.16 (d, *J* = 7.7 Hz, 1H), 7.08 (dd, *J* = 7.7, 4.8 Hz, 1H), 6.65 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.71 (dd, *J* = 17.6, 1.0 Hz, 1H), 5.20 (dd, *J* = 10.8, 0.9 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 1H), 3.46 – 3.32 (m, 2H), 3.16 – 3.09 (m, 2H), 2.90 – 2.79 (m, 2H), 2.52 – 2.28 (m, 4H), 2.40 – 2.28 (m, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). All data are in accordance with the literature.[22]

5. Experimental Procedures and Characterization of Products

5.1 General procedure for photocatalyzed carboxylative alkylation of styrenes

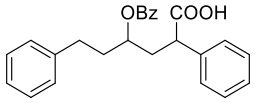


In glovebox, an oven-dried 8.0 mL vial with a stirring bar was added with $ZnBr_2$ (0.02 mmol, 10 mol%), followed by the addition of DCM (0.20 mL) and benzoyl bromide (0.21 mmol, 1.05 eq.). The mixture was stirred for 10 min at room temperature. To the mixture, aldehyde (0.20 mmol, 1.0 eq.) was added and the resulting mixture was stirred for 2 h at room temperature. After reaction completed, the mixture was filtered through a pad of neutral Al_2O_3 and the solvent was removed in *vacuo* to afford **1'** without further purification. In glovebox, an oven-dried 25 mL Schlenk tube with obtained **1'** was added 3DPAFIPN (6.5 mg, 0.01 mmol, 5 mol%), K_3PO_4 (42.0 mg, 0.2 mmol, 1.0 eq.) and 5 Å MS (100.0 mg). The tube was removed from glovebox, then evacuated and back-filled with CO_2 for 3 times. To the tube was added DMA (2.0 mL), alkene (0.60 mmol, 3.0 eq. if liquid) and TMEDA (90 μL, 0.60 mmol, 3.0 eq.) under CO_2 atmosphere at room temperature. The tube was then charged with CO_2 at −78 °C for another 2 minutes and stirred at –10 °C under blue LEDs (455 nm, 15W) irradiation for 12 h. The resulting mixture was diluted with 2.0 mL of EA and quenched by 2.0 mL of 2 M HCl (aq.). After stirring for 15 min at room temperature, the mixture was extracted with EA, and the combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was dissolved in Et_2O (2.0 mL) and MeOH (0.5 mL), and a Et_2O solution of $TMSCHN_2$ (2.0 eq.) was added at 0 °C. The mixture was stirred at 0 °C for 30 min and the solvent was removed under reduced pressure. The crude material was purified by flash column chromatography on silica gel to provide the desired product.

Note: When the crude mixture 1' was used directly or simply concentrated without filtration, the yield of product was decreased. Therefore, it is necessary to filter through a pad of neutral Al_2O_3 and concentrate in *vacuo* to get higher yield.

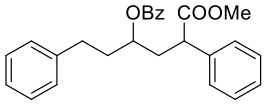
5.2 Characterization of products

4-(Benzoyloxy)-2,6-diphenylhexanoic acid (3)



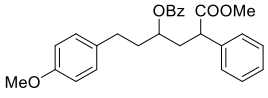
According to general procedure except for the step of subsequent esterification, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA: CH_3COOH = 2: 1: 0.5%) to afford 55.1 mg (71% yield, 61:39 dr) of **3** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.00 – 7.93 (m, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.31 – 7.19 (m, 7H), 7.16 – 7.08 (m, 3H), 5.27 – 5.21 (m, 0.6H), 5.07 – 5.01 (m, 0.4H), 3.70 (ddd, *J* = 18.0, 8.8, 5.8 Hz, 1H), 2.75 – 2.53 (m, 3H), 2.22 – 1.87 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 179.71, 179.18, 166.27, 166.13, 141.33, 141.25, 138.21, 137.70, 133.12, 133.03, 130.23, 130.21, 129.68, 129.00, 128.94, 128.55, 128.51, 128.46, 128.39, 128.38, 128.35, 128.29, 128.02, 127.90, 127.74, 126.09, 126.06, 72.91, 72.49, 48.36, 47.94, 37.50, 37.42, 36.46, 36.09, 31.66, 31.49. HRMS m/z (ESI) calculated for $C_{25}H_{24}O_4$ $(M + H)^+$ 389.1747, found 389.1754.

6-Methoxy-6-oxo-1,5-diphenylhexan-3-yl benzoate (4)



According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to afford 59.5 mg (74% yield, 62:38 dr) of **4** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 7.5 Hz, 0.8H), 7.91 (d, *J* = 7.0 Hz, 1.2H), 7.47 (q, *J* = 6.8 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.22 – 7.12 (m, 7H), 7.07 – 7.01 (m, 3H), 5.19 – 5.14 (m, 0.6H), 5.03 – 4.98 (m, 0.4H), 3.66 – 3.61 (m, 1H), 3.50 (s, 1.8H), 3.37 (s, 1.2H), 2.68 – 2.49 (m, 3H), 2,13 – 1.81 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.20, 173.83, 166.22, 166.06, 141.40, 141.28, 138.88, 138.50, 133.10, 133.01, 130.34, 130.28, 129.75, 129.68, 128.92, 128.87, 128.51, 128.48, 128.41, 128.37, 128.34, 128.03, 127.78, 127.62, 127.49, 126.04, 126.02, 72.87, 72.67, 52.23, 52.08, 48.34, 47.97, 38.15, 37.97, 36.49, 36.37, 31.68, 31.52. HRMS m/z (ESI) calculated for $C_{26}H_{26}O_4$ $(M + H)^+$ 403.1904, found 403.1906.

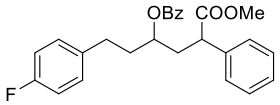
6-Methoxy-1-(4-methoxyphenyl)-6-oxo-5-phenylhexan-3-yl benzoate (5)



According to general procedure, the reaction was carried out with **1b** (32.8 mg, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 15: 1) to afford 50.9 mg (59% yield, 65:35 dr) of **5** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 6.8 Hz, 0.7H), 7.90 (d, *J* = 6.8 Hz, 1.3H), 7.51

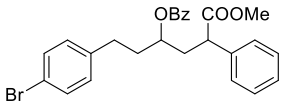
– 7.46 (m, 1H), 7.36 (q, *J* = 8.3 Hz, 2H), 7.23 – 7.12 (m, 5H), 7.00 – 6.93 (m, 2H), 6.72 – 6.68 (m, 2H), 5.19 – 5.14 (m, 0.6H), 5.02 – 4.96 (m, 0.4H), 3.67 – 3.59 (m, 4H), 3.52 (s, 2H), 3.39 (s, 1H), 2.61 – 2.48 (m, 3H), 2.14 – 1.77 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.27, 173.88, 166.68, 166.11, 157.97, 138.93, 138.55, 133.49, 133.36, 133.11, 133.02, 130.40, 130.33, 129.78, 129.71, 129.30, 129.27, 128.94, 128.89, 128.49, 128.42, 128.06, 127.82, 127.64, 127.51, 113.96, 113.93, 72.91, 72.71, 55.33, 52.27, 52.13, 48.37, 47.99, 38.18, 38.01, 36.72, 36.61, 30.81, 30.65. HRMS m/z (ESI) calculated for $C_{27}H_{28}O_5$ $(M + Na)^+$ 455.1829, found 455.1830.

1-(4-Fluorophenyl)-6-methoxy-6-oxo-5-phenylhexan-3-yl benzoate (6)



According to general procedure, the reaction was carried out with **1c** (28 μL, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to afford 50.5 mg (60 % yield, 60:40 dr) of **6** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 7.0 Hz, 0.8H), 7.90 (d, *J* = 7.0 Hz, 1.2H), 7.47 (q, *J* = 6.8 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.22 – 7.10 (m, 5H), 7.01 – 6.94 (m, 2H), 6.85 – 6.78 (m, 2H), 5.17 – 5.12 (m, 0.6H), 4.99 – 4.94 (m, 0.4H), 3.65 – 3.60 (m, 1H), 3.50 (s, 1.8H), 3.38 (s, 1.2H), 2.60 – 2.47 (m, 3H), 2.12 – 1.78 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.19, 173.81, 166.22, 166.06, 161.40 (d, *J* = 244.4 Hz), 161.40 (d, *J* = 244.4 Hz), 138.83, 138.45, 136.93 (d, *J* = 13.7 Hz), 136.89 (d, *J* = 13.7 Hz), 133.16, 133.08, 130.27, 130.21, 129.74 (d, *J* = 7.8 Hz), 129.70 (d, *J* = 6.8 Hz), 128.94, 128.89, 128.50, 128.43, 128.02, 127.77, 127.65, 127.52, 115.24 (d, *J* = 21.2 Hz), 115.21 (d, *J* = 21.1 Hz), 72.70, 72.46, 52.25, 52.11, 48.31, 47.96, 38.17, 37.98, 36.54, 36.45, 30.90, 30.72. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -117.44, -117.47. HRMS m/z (ESI) calculated for $C_{26}H_{25}FO_4$ $(M + H)^+$ 421.1810, found 421.1819.

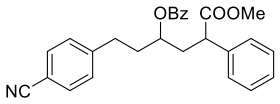
1-(4-Bromophenyl)-6-methoxy-6-oxo-5-phenylhexan-3-yl benzoate (7)



According to general procedure, the reaction was carried out with **1d** (31 μL, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to afford 65.3 mg (68% yield, 60:40 dr) of **7** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 8.0 Hz, 0.8H), 7.89 (d, *J* = 7.5 Hz, 1.2H), 7.49 (q, *J* = 6.8 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.28 – 7.12 (m, 7H), δ 6.94 (d, *J* = 8.5 Hz, 1.2H), 6.89 (d, *J* = 8.0 Hz, 0.8H), 5.17 – 5.12 (m, 0.6H), 4.99 – 4.94 (m, 0.4H), 3.65 – 3.60 (m, 1H), 3.52 (s, 1.8H), 3.40 (s, 1.2H), 2.62 – 2.47 (m, 3H), 2.13 – 1.78 (m, 3H).

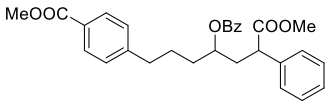
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.18, 173.82, 166.23, 166.09, 140.39, 140.24, 138.83, 138.45, 133.20, 133.11, 131.60, 131.56, 130.27, 130.21, 130.19, 130.15, 129.76, 129.69, 128.97, 128.92, 128.53, 128.46, 128.05, 127.80, 127.69, 127.55, 119.85, 119.83, 72.71, 72.46, 52.28, 52.14, 48.34, 48.01, 38.20, 38.02, 36.22, 36.16, 31.19, 31.01. HRMS m/z (ESI) calculated for $C_{26}H_{25}BrO_4$ $(M + H)^+$ 481.1009, found 481.1013.

1-(4-Cyanophenyl)-6-methoxy-6-oxo-5-phenylhexan-3-yl benzoate (8)



According to general procedure, the reaction was carried out with **1e** (29 μL, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 15: 1) to afford 55.5 mg (65% yield, 58:42 dr) of **8** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 7.7 Hz, 0.8H), 7.95 (d, *J* = 7.7 Hz, 1.2H), 7.58 (q, *J* = 7.0 Hz, 1H), 7.52 – 7.42 (m, 4H), 7.32 – 7.18 (m, 7H), 5.25 – 5.21 (m, 0.6H), 5.06 – 5.01 (m, 0.4H), 3.73 – 3.67 (m, 1H), 3.60 (s, 2H), 3.48 (s, 1H), 2.79 – 2.55 (m, 3H), 2.20 – 1.91 (m, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.09, 173.74, 166.17, 166.02, 147.01, 146.87, 138.67, 138.29, 133.31, 133.23, 132.33, 132.29, 130.01, 129.95, 129.70, 129.62, 129.22, 129.17, 128.97, 128.91, 128.52, 128.46, 127.99, 127.72, 127.57, 119.03, 119.02, 109.98, 109.95, 72.47, 72.15, 52.29, 52.15, 48.23, 47.91, 38.19, 37.95, 35.73, 35.68, 31.92, 31.72. HRMS m/z (ESI) calculated for $C_{27}H_{25}NO_4$ $(M + H)^+$ 428.1856, found 428.1855.

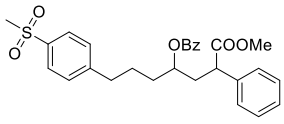
Methyl 4-(4-(benzoyloxy)-7-methoxy-7-oxo-6-phenylheptyl)benzoate (9)



According to general procedure, the reaction was carried out with **1f** (41.3 mg, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 10: 1) to afford 46.8 mg (49% yield, 61:39 dr) of **9** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.03 (d, *J* = 8.0 Hz, 0.8H), 7.98 (d, *J* = 8.0 Hz, 1.2H), 7.92 (t, *J* = 8.5 Hz, 2H), 7.57 (q, *J* = 7.2 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.31 – 7.15 (m, 7H), 5.25 – 5.20 (m, 0.6H), 5.06 – 5.02 (m, 0.4H), 3.89 (s, 3H), 3.71 – 3.66 (m, 1H), 3.60 (s, 1.8H), 3.47 (s, 1.2H), 2.69 – 2.49 (m, 3H), 2.15 – 2.03 (m, 1H), 1.77 – 1.62 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.23, 173.86, 167.22, 166.28, 166.11, 147.55, 147.50, 138.90, 138.47, 133.16, 133.07, 130.34, 130.27, 129.84, 129.82, 129.77, 129.69, 128.95, 128.90, 128.57, 128.53, 128.46, 128.05, 128.00, 127.78, 127.68, 127.52, 72.57, 52.28, 52.13, 52.07, 48.38, 48.00, 38.21, 38.02, 35.65, 34.30, 34.11, 26.68, 26.58. HRMS m/z (ESI) calculated for $C_{29}H_{30}O_6$ $(M + H)^+$

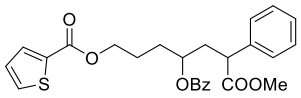
475.2115, found 475.2113.

Methoxy-7-(4-(methylsulfonyl)phenyl)-1-oxo-2-phenylheptan-4-yl benzoate (10)



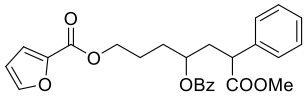
According to general procedure, the reaction was carried out with **1g** (45.2 mg, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 1: 1) to afford 53.4 mg (54% yield, 62:38 dr) of **10** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 9.0 Hz, 0.8H), 7.90 (d, *J* = 7.5 Hz, 1.2H), 7.74 (t, *J* = 8.8 Hz, 2H), 7.50 (q, *J* = 7.2 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.26 – 7.12 (m, 7H), 5.17 – 5.13 (m, 0.6H), 4.99 – 4.94 (m, 0.4H), 3.64 – 3.58 (m, 1H), 3.53 (s, 1.8H), 3.39 (m, 1.2H), 2.94 (d, *J* = 3.5 Hz, 3H), 2.65 – 2.42 (m, 3H), 2.08 – 1.96 (m, 1H), 1.72 – 1.57 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.17, 173.84, 166.28, 166.10, 148.65, 148.57, 138.83, 138.39, 138.24, 133.23, 133.14, 130.21, 130.15, 129.73, 129.66, 129.46, 129.42, 128.95, 128.90, 128.55, 128.49, 128.02, 127.73, 127.69, 127.54, 72.66, 72.37, 52.28, 52.14, 48.33, 47.96, 44.67, 38.26, 38.02, 35.51, 34.27, 34.13, 26.71, 26.57. HRMS m/z (ESI) calculated for $C_{28}H_{30}O_6S$ $(M + H)^+$ 495.1836, found 495.1831.

4-(Benzoyloxy)-7-methoxy-7-oxo-6-phenylheptyl thiophene-2-carboxylate (11)



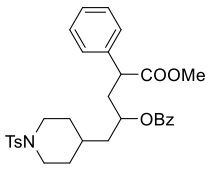
According to general procedure, the reaction was carried out with **1h** (39.6 mg, 0.2mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 7: 1) to afford 45.7 mg (49% yield, 60:40 dr) of **11** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.04 (d, *J* = 7.0 Hz, 0.8H), 7.99 (d, *J* = 8.0 Hz, 1.2H), 7.78 (dd, *J* = 8.8, 1.3 Hz, 0.6H), 7.75 (dd, *J* = 8.8, 1.3 Hz, 0.4H), 7.59 – 7.52 (m, 2H), 7.47 – 7.42 (m, 2H), 7.32 – 7.19 (m, 5H), 7.09 (q, *J* = 14.0 Hz, 1H), 5.28 – 5.23 (m, 0.6H), 5.11 – 5.07 (m, 0.4H), 4.31 – 4.24 (m, 2H), 3.74 – 3.69 (m, 1H), 3.61 (s, 1.8H), 3.47 (s, 1.2H), 2.66 – 2.54 (m, 1H), 2.19 – 2.10 (m, 1H),1.88 – 1.78 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.20, 173.85, 166.25, 166.09, 162.29, 162.25, 138.82, 138.45, 133.92, 133.89, 133.53, 133.50, 133.21, 133.12, 132.45, 130.26, 130.19, 129.81, 129.73, 128.98, 128.93, 128.54, 128.48, 128.05, 127.86, 127.84, 127.81, 127.71, 127.57, 72.69, 72.46, 64.77, 64.74, 52.32, 52.16, 48.40, 48.02, 38.16, 38.00, 31.34, 31.15, 24.72, 24.59. HRMS m/z (ESI) calculated for $C_{26}H_{26}O_6S$ $(M + H)^+$ 467.1523, found 467.1522.

4-(Benzoyloxy)-7-methoxy-7-oxo-6-phenylheptyl furan-2-carboxylate (12)



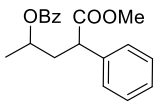
According to general procedure, the reaction was carried out with **1i** (36.4 mg, 0.2mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 7: 1) to afford 32.4 mg (36% yield, 60:40 dr) of **12** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.03 (dd, *J* = 8.0, 1.5 Hz, 0.8H), 7.99 (dd, *J* = 8.3, 1.3 Hm, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.20, 173.85, 166.26, 166.10, 158.80, 158.77, 146.41, 144.78, 138.83, 138.44, 133.23, 133.14, 130.25, 130.18, 129.81, 129.74, 128.99, 128.93, 128.55, 128.49, 128.06, 127.81, 127.72, 127.57, 118.05, 118.03, 111.95, 72.68, 72.42, 64.60, 64.57, 52.33, 52.17, 48.40, 48.03, 38.18, 38.01, 31.31, 31.13, 24.71, 24.58. HRMS m/z (ESI) calculated for $C_{26}H_{26}O_7$ $(M + H)^+$ 451.1751, found 451.1753.

5-Methoxy-5-oxo-4-phenyl-1-(1-tosylpiperidin-4-yl)pentan-2-yl benzoate (13)



According to general procedure, the reaction was carried out with **1j** (56.2 mg, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 1: 1) to afford 50.5 mg (46% yield, 60:40 dr) of **13** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.90 (d, *J* = 7.0 Hz, 0.8H), 7.86 (d, *J* = 7.0 Hz, 1.2H), 7.53 – 7.46 (m, 3H), 7.38 – 7.33 (m, 2H), 7.22 – 7.11 (m, 7H), 5.18 – 5.13 (m, 0.6H), 5.04 – 4.99 (m, 0.4H), 3.66 – 3.56 (m, 3H), 3.51 (s, 1.8H), 3.49 (s, 1.2H), 2.49 – 2.37 (m, 1H), 2.33 (s, 3H), 2.12 – 1.91 (m, 3H),1.76 – 1.58 (m, 3H), 1.49 – 1.18 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.09, 173.77, 166.14, 166.02, 143.47, 138.67, 138.43, 133.23, 133.15, 133.09, 133.07, 130.11, 130.04, 129.74, 129.67, 128.92, 128.89, 128.52, 128.47, 127.95, 127.81, 127.79, 127.73, 127.69, 127.56, 70.66, 70.59, 52.27, 52.09, 48.34, 47.86, 46.38, 46.35, 46.30, 41.52, 41.30, 38.66, 31.97, 31.89, 31.85, 31.74, 31.27, 21.59. HRMS m/z (ESI) calculated for $C_{31}H_{35}NO_6S$ $(M + H)^+$ 550.2258, found 550.2260.

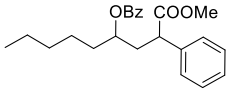
5-Methoxy-5-oxo-4-phenylpentan-2-yl benzoate (14)



According to general Procedure, the reaction was carried out with **1k** (11 μL, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 40: 1) to afford 41.5 mg (67% yield, 60:40 dr) of **14** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 6.8 Hz, 0.8H), 8.03 (d, *J* = 7.2 Hz, 1.2H), 7.64 – 7.58 (m, 1H), 7.52 – 7.46 (m, 2H), 7.37 – 7.27 (m, 5H), 5.27 – 5.20 (m, 0.6H), 5.08 – 5.00 (m, 0.4H), 3.83 – 3.77

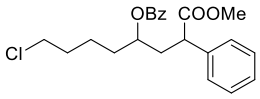
(m, 1H), 3.67 (s, 1.8H), 3.58 (s, 1.2H), 2.69 – 2.53 (m, 1H), 2.24 – 2.14 (m, 1H), 1.41 (dd, *J* = 19.2, 6.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.25, 173.93, 166.13, 165.98, 138.91, 138.52, 133.04, 132.95, 130.65, 130.58, 129.73, 129.66, 128.97, 128.92, 128.47, 128.40, 128.04, 127.87, 127.65, 127.54, 70.07, 69.86, 52.26, 52.15, 48.48, 48.14, 39.86, 39.83, 20.58, 20.44. HRMS m/z (ESI) calculated for $C_{19}H_{20}O_4$ $(M + H)^+$ 313.1434, found 313.1436.

1-Methoxy-1-oxo-2-phenylnonan-4-yl benzoate (15)



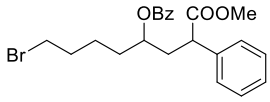
According to general procedure, the reaction was carried out with **1l** (16.8 mg, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 30: 1) to afford 29.5 mg (40% yield, 60:40 dr) of **15** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 6.8 Hz, 0.8H), 7.92 (d, *J* = 7.2 Hz, 1.2H), 7.52 – 7.46 (m, 1H), 7.37 (q, *J* = 8.0 Hz, 2H), 7.25 – 7.12 (m, 5H), 5.14 – 5.08 (m, 0.6H), 4.97 – 4.90 (m, 0.4H), 3.67 – 3.54 (m, 3H), 3.40 (s, 1H), 2.53 – 2.45 (m, 1H), 2.11 – 1.96 (m, 1H), 1.71 – 1.48 (m, 2H), 1.31 – 1.14 (m, 6H), 0.85 – 0.74 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.40, 173.99, 166.33, 166.15, 139.10, 138.66, 133.05, 132.97, 130.58, 130.51, 129.78, 129.71, 128.94, 128.89, 128.50, 128.43, 128.09, 127.84, 127.63, 127.49, 73.37, 73.20, 52.28, 52.13, 48.48, 48.06, 38.20, 37.97, 34.78, 34.61, 31.78, 31.76, 24.93, 24.81, 22.62, 22.59, 14.13, 14.11. HRMS m/z (ESI) calculated for $C_{23}H_{28}O_4$ $(M + H)^+$ 369.2060, found 369.2060.

8-Chloro-1-methoxy-1-oxo-2-phenyloctan-4-yl benzoate (16)



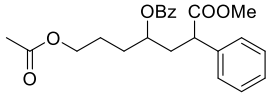
According to general procedure, the reaction was carried out with **1m** (24.0 mg, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to afford 49.5 mg (64% yield, 58:42 dr) of **16** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 7.5 Hz, 0.8H), 7.91 (d, *J* = 7.0 Hz, 1.2H), 7.50 (q, *J* = 7.0 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.25 – 7.12 (m, 5H), 5.15 – 5.10 (m, 0.6H), 4.96 – 4.91 (m, 0.4H), 3.66 – 3.60 (m, 1H), 3.54 (s, 1.8H), 3.45 – 3.38 (m, 3.2H), 2.54 – 2.45 (m, 1H), 2.10 – 1.98 (m, 1H), 1.75 – 1.37 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.25, 173.88, 166.29, 166.11, 138.94, 138.48, 133.17, 133.08, 130.35, 130.29, 129.78, 129.71, 128.97, 128.92, 128.53, 128.47, 128.06, 127.80, 127.69, 127.54, 72.86, 72.64, 52.30, 52.15, 48.41, 48.02, 44.78, 44.75, 38.14, 37.90, 34.01, 33.85, 32.35, 22.56, 22.45. HRMS m/z (ESI) calculated for $C_{22}H_{25}ClO_4$ $(M + H)^+$ 389.1514, found 389.1512.

8-Bromo-1-methoxy-1-oxo-2-phenyloctan-4-yl benzoate (17)



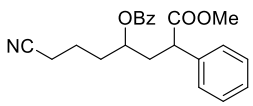
According to general procedure, the reaction was carried out with **1n** (32.8 mg, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to afford 36.2 mg (42% yield, 55:45 dr) of **17** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.96 (dd, *J* = 8.4, 1.6 Hz, 0.9H), 7.91 (dd, *J* = 8.4, 1.5 Hz, 1.1H), 7.52 – 7.47 (m, 1H), 7.41 – 7.35 (m, 2H), 7.24 – 7.13 (m, 5H), 5.15 – 5.09 (m, 0.5H), 4.97 – 4.90 (m, 0.5H), 3.67 – 3.60 (m, 1H), 3.54 (s, 1.6H), 3.41 (s, 1.4H), 3.32 – 3.25 (m, 2H), 2.55 – 2.44 (m, 1H), 2.11 – 1.97 (m, 1H), 1.82 – 1.38 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.26, 173.89, 166.30, 166.12, 138.94, 138.48, 133.18, 133.09, 130.36, 130.29, 129.79, 129.72, 128.98, 128.93, 128.54, 128.48, 128.07, 127.81, 127.70, 127.55, 72.84, 72.61, 52.32, 52.17, 48.42, 48.02, 38.14, 37.90, 33.86, 33.70, 33.48, 33.43, 32.49, 23.82, 23.71. HRMS m/z (ESI) calculated for $C_{22}H_{25}BrO_4$ $(M + H)^+$ 433.1009, found 433.1013.

7-Acetoxy-1-methoxy-1-oxo-2-phenylheptan-4-yl benzoate (18)



According to general procedure, the reaction was carried out with **1o** (26.0 mg, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 8: 1) to afford 34.1 mg (43% yield, 60:40 dr) of **18** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.97 (dd, *J* = 8.3, 1.4 Hz, 0.8H), 7.92 – 7.91 (m, 1.2H), 7.53 – 7.46 (m, 1H), 7.40 – 7.35 (m, 2H), 7.25 – 7.12 (m, 5H), 5.17 – 5.13 (m, 0.6H), 5.00 – 4.95 (m, 0.4H), 3.99 (t, *J* = 6.3 Hz, 1.2H), 3.94 (t, *J* = 6.3 Hz, 0.8H), 3.66 – 3.60 (m, 1H), 3.54 (s, 1.8H), 3.40 (s, 1.2H), 2.56 – 2.45 (m, 1H), 2.10 – 1.99 (m, 1H), 1.95 (s, 1.8H), 1.92 (s, 1.2H), 1.74 – 1.56 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.18, 173.83, 171.16, 171.13, 166.22, 166.05, 138.85, 138.43, 133.19, 133.10, 130.25, 130.18, 129.77, 129.69, 128.96, 128.90, 128.52, 128.46, 128.03, 127.77, 127.69, 127.54, 72.67, 72.41, 64.14, 64.11, 52.29, 52.14, 48.36, 47.99, 38.19, 37.97, 31.35, 31.20, 24.55, 24.41, 21.03, 21.00. HRMS m/z (ESI) calculated for $C_{23}H_{26}O_6$ $(M + H)^+$ 399.1802, found 399.1806.

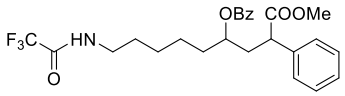
7-Cyano-1-methoxy-1-oxo-2-phenylheptan-4-yl benzoate (19)



According to general procedure, the reaction was carried out with **1p** (20 μL, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product

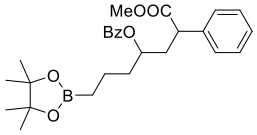
was purified by flash column chromatography on silica gel (PE: EA = 10: 1) to afford 29.2 mg (40% yield, 62:38 dr) of **19** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.05 – 8.02 (m, 0.8H), 8.00 – 7.97 (m, 1.2H), 7.60 – 7.56 (m, 1H), 7.49 – 7.43 (m, 2H), 7.32 – 7.22 (m, 5H), 5.25 – 5.19 (m, 0.6H), 5.07 – 5.02 (m, 0.4H), 3.73 – 3.67 (m, 1H), 3.62 (s, 1.9H), 3.49 (s, 1.1H), 2.65 – 2.51 (m, 1H), 2.39 – 2.30 (m, 2H), 2.17 – 2.08 (m, 1H), 1.90 – 1.67 (m, 4H) **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.03, 173.73, 166.24, 166.09, 138.62, 138.21, 133.39, 133.29, 129.92, 129.86, 129.79, 129.71, 129.02, 128.96, 128.60, 128.54, 128.01, 127.79, 127.75, 127.63, 119.33, 119.27, 71.91, 71.57, 52.34, 52.20, 48.27, 47.94, 38.24, 38.05, 33.84, 33.65, 21.50, 21.34, 17.08, 17.05. HRMS m/z (ESI) calculated for $C_{22}H_{23}NO_4$ $(M + H)^+$ 366.1700, found 366.1702.

1-Methoxy-1-oxo-2-phenyl-8-(2,2,2-trifluoroacetamido)octan-4-yl benzoate (20)



According to general procedure, the reaction was carried out with **1q** (41.8 mg, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 1: 1) to afford 31.6 mg (33% yield, 59:41 dr) of **20** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.03 (d, J = 8.0 Hz, 0.9H), 7.98 (d, J = 8.0 Hz, 1.1H), 7.57 (q, J = 7.0 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.32 – 7.21 (m, 5H), 6.57 – 6.51 (m, 1H), 5.22 – 5.17 (m, 0.6H), 5.03 – 4.98 (m, 0.4H), 3.73 – 3.67 (m, 1H), 3.61 (s, 1.7H), 3.48 (s, 1.3H), 3.39 – 3.20 (m, 2H), 2.60 – 2.51 (m, 1H), 2.16 – 2.03 (m, 1H), 1.79 – 1.26 (m, 8H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.28, 173.97, 166.49, 166.31, 157.35 (q, J = 40.4 Hz), 157.33 (q, J = 38.4 Hz), 138.91, 138.46, 133.25, 133.16, 130.28, 130.21, 129.76, 129.69, 128.96, 128.92, 128.57, 128.51, 128.05, 127.78, 127.70, 127.55, 116.02 (q, J = 288.3 Hz), 116.00 (q, J = 289.1 Hz),72.84, 72.61, 52.29, 52.16, 48.43, 48.04, 39.67, 38.26, 38.05, 34.60, 34.44, 28.75, 28.70, 26.15, 26.11, 24.59, 24.47. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -75.89, -75.91. HRMS m/z (ESI) calculated for $C_{24}H_{26}F_3NO_5$ $(M + Na)^+$ 502.1812, found 502.1802.

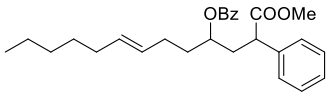
1-Methoxy-1-oxo-2-phenyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-4-yl benzoate (21)



According to general procedure, the reaction was carried out with **1r** (39.6 mg, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 10: 1) to afford 41.1 mg (44% yield, 58:42 dr) of **21** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.02 (d, J = 7.0 Hz, 0.9H), 7.98 (d, J = 7.0 Hz, 1.1H), 7.57 – 7.53

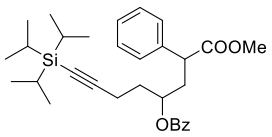
(m, 1H), 7.46 – 7.41 (m, 2H), 7.31 – 7.19 (m, 5H), 5.18 – 5.13 (m, 0.6H), 5.04 – 4.99 (m, 0.4H), 3.74 – 3.67 (m, 1H), 3.60 (s, 1.7H), 3.46 (s, 1.3H), 2.61 – 2.52 (m, 1H), 2.17 – 2.06 (m, 1H), 1.79 – 1.63 (m, 2H), 1.57 – 1.40 (m, 2H), 1.21 (d, J = 7.5 Hz, 12H), 0.80 – 0.73 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.37, 173.96, 166.23, 166.07, 139.07, 138.72, 132.96, 132.87, 130.66, 130.58, 129.79, 129.73, 128.90, 128.85, 128.42, 128.36, 128.07, 127.86, 127.57, 127.46, 83.10, 83.09, 73.25, 73.16, 52.23, 52.08, 48.49, 48.01, 37.89, 37.83, 37.31, 37.03, 24.93, 24.91, 19.59, 19.50. HRMS m/z (ESI) calculated for $C_{27}H_{35}BO_6$ $(M + H)^+$ 467.2599, found 467.2599.

(*E*)-1-Methoxy-1-oxo-2-phenyltridec-7-en-4-yl benzoate (22)



According to general procedure, the reaction was carried out with **1s** (30.8 mg, 0.2mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to afford 39.7 mg (47% yield, 62:38 dr) of **22** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.04 (dd, J = 8.3, 1.3 Hz, 0.8H), 8.00 (dd, J = 8.3, 1.3 Hz, 1.2H), 7.58 – 7.53 (m, 1H), 7.46 – 7.41 (m, 2H), 7.32 – 7.19 (m, 5H), 5.39 – 5.25 (m, 2H), 5.23 – 5.18 (m, 0.6H), 5.07 – 5.02 (m, 0.4H), 3.74 – 3.69 (m, 2.7H), 3.60 (s, 1.8H), 3.47 (s, 1.2H), 2.62 – 2.54 (m, 1H), 2.18 – 2.04 (m, 3H), 1.97 – 1.90 (m, 2H), 1.82 – 1.64 (m, 2H), 1.32 – 1.16 (m, 6H), 0.85 (t, J = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.30, 173.90, 166.24, 166.07, 139.01, 138.63, 133.05, 132.97, 131.09, 131.04, 130.49, 130.42, 129.76, 129.69, 128.92, 128.88, 128.47, 128.41, 128.26, 128.24, 128.06, 127.82, 127.62, 127.49, 72.94, 72.82, 52.25, 52.10, 48.43, 48.01, 38.16, 37.98, 34.83, 34.67, 31.59, 31.57, 29.41, 29.39, 27.28, 27.25, 23.14, 23.02, 22.63, 14.16. HRMS m/z (ESI) calculated for $C_{27}H_{34}O_4$ $(M + H)^+$ 423.2530, found 423.2529.

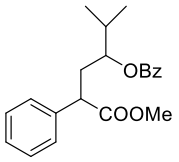
1-Methoxy-1-oxo-2-phenyl-8-(triisopropylsilyl)oct-7-yn-4-yl benzoate (23)



According to general procedure, the reaction was carried out with **1t** (47.6 mg, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 15: 1) to afford 55.7 mg (55% yield, 60:40 dr) of **23** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.96 (d, J = 7.5 Hz, 0.8H), 7.91 (d, J = 7.5 Hz, 1.2H), 7.49 (q, J = 7.0 Hz, 1H),7.39 – 7.34 (m, 2H), 7.24 – 7.12 (m, 5H), 5.22 – 5.17 (m, 0.6H), 5.06 – 5.01 (m, 0.4H), 3.66 – 3.60 (m, 1H), 3.52 (s, 1.8H), 3.39 (s, 1.2H), 2.58 – 2.48 (m, 1H), 2.30 – 2.20 (m, 2H), 2.15 – 2.03 (m, 1H), 1.95 – 1.79 (m, 2H), 0.97 – 0.87 (m,

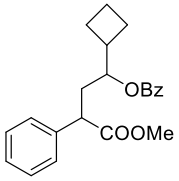
21H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.18, 173.79, 166.07, 165.92, 138.88, 138.49, 133.17, 133.08, 130.29, 130.21, 129.83, 129.75, 128.96, 128.91, 128.51, 128.45, 128.05, 127.82, 127.67, 127.54, 107.61, 107.54, 81.00, 72.35, 72.25, 52.28, 51.67, 48.42, 48.02, 38.04, 37.92, 34.35, 34.11, 18.73, 15.85, 11.34. HRMS m/z (ESI) calculated for $C_{31}H_{42}O_4Si$ $(M + H)^+$ 507.2925, found 507.2925.

6-Methoxy-2-methyl-6-oxo-5-phenylhexan-3-yl benzoate (24)



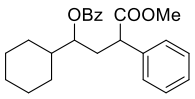
According to general procedure, the reaction was carried out with **1u** (18 μL, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to afford 38.7 mg (57% yield, 52:48 dr) of **24** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 (d, *J* = 7.2 Hz, 0.9H), 8.00 (d, *J* = 7.2 Hz, 1.1H), 7.59 – 7.41 (m, 3H), 7.33 – 7.18 (m, 5H), 5.11 – 5.06 (m, 0.5H), 4.94 – 4.90 (m, 0.5H), 3.69 – 3.60 (m, 2.7H), 3.41 (s, 1.3H), 2.59 – 2.50 (m, 1H), 2.15 – 1.90 (m, 2H), 1.02 – 0.91 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.43, 173.97, 166.38, 166.20, 139.28, 138.70, 133.05, 132.95, 130.57, 130.51, 129.81, 129.72, 128.89, 128.86, 128.51, 128.43, 128.17, 127.79, 127.62, 127.43, 52.23, 52.02, 48.59, 48.22, 35.54, 34.94, 32.28, 32.18, 18.50, 18.15, 17.88, 17.75. HRMS m/z (ESI) calculated for $C_{21}H_{24}O_4$ $(M + H)^+$ 341.1747, found 341.1748.

1-Cyclobutyl-4-methoxy-4-oxo-3-phenylbutyl benzoate (25)



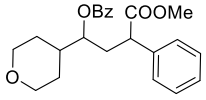
According to general procedure, the reaction was carried out with **1v** (18 μL, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to afford 33.7 mg (47% yield, 58:42 dr) of **25** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.02 (dd, *J* = 8.3, 1.3 Hz, 0.9H), 7.97 (d, *J* = 8.0, 1.5 Hz, 1.1H), 7.55 – 7.50 (m, 1H), 7.44 – 7.38 (m, 2H), 7.29 – 7.13 (m, 5H), 5.19 – 5.15 (m, 0.6H), 5.02 – 4.98 (m, 0.4H), 3.64 – 3.58 (m, 2.7H), 3.39 (s, 1.3H), 2.62 – 2.37 (m, 2H), 2.03 – 1.62 (m, 7H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.36, 173.95, 166.56, 166.40, 139.14, 138.69, 133.05, 132.96, 130.54, 130.46, 129.82, 129.74, 128.90, 128.85, 128.50, 128.43, 128.13, 127.80, 127.62, 127.44, 75.93, 75.64, 52.85, 52.08, 48.34, 47.95, 39.73, 39.43, 36.09, 35.95, 24.51, 24.34, 18.48, 18.05. HRMS m/z (ESI) calculated for $C_{22}H_{24}O_4$ $(M + H)^+$ 353.1747, found 353.1748.

1-Cyclohexyl-4-methoxy-4-oxo-3-phenylbutyl benzoate (26)



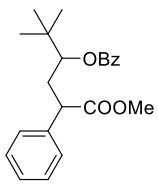
According to general procedure, the reaction was carried out with **1w** (19 mg, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 40: 1) to afford 47.1 mg (62% yield, 62:38 dr) of **26** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 7.2 Hz, 0.7H), 7.93 (d, *J* = 6.8 Hz, 1.3H), 7.53 – 7.48 (m, 1H), 7.41 – 7.35 (m, 2H), 7.26 – 7.10 (m, 5H), 5.08 – 5.04 (m, 0.6H), 4.91 – 4.86 (m, 0.4H), 3.94 – 3.85 (m, 2H), 3.63 – 3.55 (m, 2.8H), 3.34 – 3.20 (m, 3.2H), 2.55 – 2.47 (m, 1H), 2.11 – 1.92 (m, 1H), 1.90 – 1.73 (m, 1H), 1.63 – 1.13 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.27, 173.84, 166.30, 166.13, 139.04, 138.47, 133.25, 133.15, 130.13, 130.06, 129.81, 129.73, 128.94, 128.90, 128.56, 128.49, 128.09, 127.72, 127.71, 127.52, 75.82, 75.53, 67.90, 67.86, 67.73, 67.70, 52.31, 52.08, 48.38, 48.00, 39.80, 39.56, 35.57, 35.23, 29.02, 28.81, 28.16, 28.09. HRMS m/z (ESI) calculated for $C_{24}H_{28}O_4$ $(M + Na)^+$ 403.1880, found 403.1880.

4-Methoxy-4-oxo-3-phenyl-1-(tetrahydro-2*H*-pyran-4-yl)butyl benzoate (27)



According to general procedure, the reaction was carried out with **1x** (22.8 mg, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 15: 1) to afford 45.8 mg (60% yield, 55:45 dr) of **27** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 7.2 Hz, 0.9H), 7.93 (d, *J* = 6.8 Hz, 1.1H), 7.52 – 7.47 (m, 1H), 7.41 – 7.35 (m, 2H), 7.26 – 7.10 (m, 6H), 5.03 – 4.99 (m, 0.5H), 4.86 – 4.82 (m, 0.5H), 3.62 – 3.53 (m, 2.6H), 3.34 (s, 1.4H), 2.53 – 2.45 (m, 1H), 2.11 – 1.92 (m, 1H), 1.75 – 1.52 (m, 6H), 1.19 – 0.93 (m, 5H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.46, 173.99, 166.37, 166.20, 139.31, 138.71, 133.05, 132.95, 130.55, 130.48, 129.83, 129.74, 128.88, 128.85, 128.51, 128.44, 128.15, 127.78, 127.60, 127.41, 52.24, 52.03, 48.59, 48.18, 42.28, 42.05, 35.70, 35.29, 29.01, 28.71, 28.31, 28.21, 26.48, 26.45, 26.18, 26.16. HRMS m/z (ESI) calculated for $C_{23}H_{26}O_5$ $(M + H)^+$ 383.1853, found 383.1857.

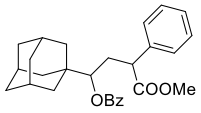
6-Methoxy-2,2-dimethyl-6-oxo-5-phenylhexan-3-yl benzoate (28)



According to general procedure, the reaction was carried out with **1y** (22 μL, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 20: 1, then PE: DCM: = 2: 1) to afford 18.5 mg (26 % yield, 55:45 dr) of **28** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 8.4 Hz, 1.1H), 8.02 (d, *J* = 7.8 Hz, 0.9H), 7.60 – 7.55 (m, 1H), 7.49 – 7.42 (m, 2H), 7.35 – 7.17 (m, 6H), 5.10 (dd, *J* = 11.2,

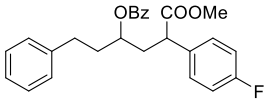
1.6 Hz, 0.6H), 4.91 (dd, *J* = 9.6, 2.0 Hz, 0.4H), 3.68 (s, 1.7H), 3.62 – 3.56 (m, 1H), 3.33 (s, 1.3H), 2.66 – 2.48 (m, 1H), 2.22 – 2.14 (m, 0.5H), 1.94 – 1.86 (m, 0.5H), 1.00 (s, 5.0H), 0.92 (s, 4.0H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.52, 173.97, 166.53, 166.37, 139.50, 138.76, 133.09, 132.99, 130.45, 130.42, 129.88, 129.80, 128.84, 128.58, 128.56, 128.47, 128.30, 127.74, 127.61, 127.37, 79.65, 79.45, 52.26, 51.94, 48.70, 48.41, 35.26, 35.18, 34.50, 34.03, 26.08, 25.99. HRMS m/z (ESI) calculated for $C_{22}H_{26}O_4$ $(M + H)^+$ 355.1904, found 355.1902.

1-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-4-methoxy-4-oxo-3-phenylbutyl benzoate (29)



According to general procedure, the reaction was carried out with **1z** (32.9 mg, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to afford 18.0 mg (21 % yield, 59:41 dr) of **29** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 (dd, *J* = 6.8 Hz, 0.9H), 7.95 (d, *J* = 7.4 Hz, 1.1H), 7.51 – 7.46 (m, 1H), 7.41 – 7.34 (m, 2H), 7.27 – 7.06 (m, 5H), 4.87 (d, *J* = 10.8 Hz, 0.6H), 4.68 (d, *J* = 9.2 Hz, 0.4H), 3.58 (s, 1.7H), 3.53 – 3.46 (m, 1H), 3.25 (s, 1.3H), 2.55 – 2.40 (m, 1H), 2.13 – 1.74 (m, 6H), 1.64 – 1.43 (m, 10H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.53, 173.97, 166.53, 166.37, 139.55, 138.77, 133.02, 132.92, 130.49, 130.46, 129.89, 129.80, 128.79, 128.54, 128.45, 128.28, 127.72, 127.55, 127.31, 79.91, 79.68, 52.20, 51.89, 48.64, 48.35, 38.22, 38.12, 37.13, 37.05, 37.02, 36.93, 33.05, 32.52, 28.30, 28.17. HRMS m/z (ESI) calculated for $C_{28}H_{32}O_4$ $(M + H)^+$ 433.2373, found 433.2374.

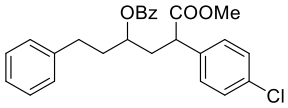
5-(4-Fluorophenyl)-6-methoxy-6-oxo-1-phenylhexan-3-yl benzoate (30)



According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2b** (72 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to afford 42.0 mg (50% yield, 65:35 dr) of **30** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 8.0 Hz, 0.7H), 7.90 (d, *J* = 6.5 Hz, 1.3H), 7.52 – 7.48 (m, 1H), 7.40 – 7.35 (m, 2H), 7.19 – 7.03 (m, 7H), 6.93 – 6.85 (m, 2H), 5.17 – 5.12 (m, 0.7H), 5.01 – 4.96 (m, 0.3H), 3.65 – 3.60 (m, 1H), 3.53 (s, 2H), 3.41 (s, 1H), 2.68 – 2.44 (m, 3H), 2.11 – 1.82 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.13, 173.77, 166.25, 166.12, 162.33 (d, *J* = 247.1 Hz), 162.23 (d, *J* = 247.0 Hz), 141.39, 141.24, 134.55 (d, *J* = 3.1 Hz), 134.20 (d, *J* = 3.1 Hz), 133.21, 133.12, 130.31, 130.26, 129.74 (d, *J* = 8.8 Hz), 129.70 (d, *J* = 8.1 Hz), 129.48, 129.40, 128.58, 128.55, 128.46, 128.42, 128.38, 126.13, 115.84 (d, *J* = 21.5 Hz), 115.74 (d, *J* = 21.5 Hz), 72.81, 72.49,

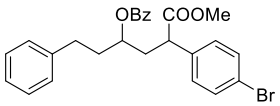
52.35, 52.21, 47.57, 47.37, 38.20, 38.11, 36.51, 36.40, 31.72, 31.59. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -114.94, -115.16. HRMS m/z (ESI) calculated for $C_{26}H_{25}FO_4$ $(M + H)^+$ 421.1810, found 421.1802.

5-(4-Chlorophenyl)-6-methoxy-6-oxo-1-phenylhexan-3-yl benzoate (31)



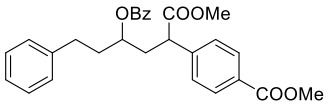
According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2c** (72 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to afford 69.8 mg (80% yield, 65:35 dr) of **31** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 8.5 Hz, 0.7H), 7.87 (d, *J* = 8.5 Hz, 1.3H), 7.52 – 7.47 (m, 1H), 7.40 – 7.34 (m, 2H), 7.20 – 7.02 (m, 9H), 5.17 – 5.12 (m, 0.7H), 5.00 – 4.95 (m, 0.3H), 3.63 – 3.59 (m, 1H), 3.52 (s, 1.9H), 3.41 (s, 1.1H), 2.67 – 2.43 (m, 3H), 2.11 – 1.82 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.87, 173.52, 166.23, 166.10, 141.34, 141.18, 137.27, 136.96, 133.60, 133.45, 133.21, 133.12, 130.24, 130.21, 129.77, 129.67, 129.49, 129.24, 129.12, 129.03, 128.58, 128.55, 128.46, 128.41, 128.37, 126.13, 72.78, 72.43, 52.38, 52.25, 47.71, 47.60, 38.02, 37.95, 36.47, 36.41, 31.70, 31.58. HRMS m/z (ESI) calculated for $C_{26}H_{25}ClO_4$ $(M + H)^+$ 437.1514, found 437.1515.

5-(4-Bromophenyl)-6-methoxy-6-oxo-1-phenylhexan-3-yl benzoate (32)



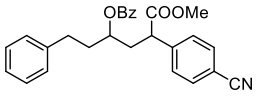
According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2d** (78 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to afford 66.2 mg (71% yield, 60:40 dr) of **32** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 7.5 Hz, 0.8H), 7.87 (d, *J* = 7.5 Hz, 1.2H), 7.52 – 7.47 (q, *J* = 7.0 Hz, 1H), 7.40 – 7.29 (m, 4H), 7.19 – 7.02 (m, 7H), 5.17 – 5.12 (m, 0.6H), 5.00 – 4.95 (m, 0.4H), 3.62 – 3.58 (m, 1H), 3.52 (s, 1.8H), 3.41 (s, 1.2H), 2.67 – 2.43 (m, 3H), 2.11 – 1.81 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.76, 173.41, 166.20, 166.07, 141.31, 141.15, 137.77, 137.47, 133.20, 133.11, 132.05, 131.97, 130.20, 130.17, 129.83, 129.75, 129.64, 129.59, 128.56, 128.54, 128.52, 128.44, 128.39, 128.35, 126.11, 121.70, 121.53, 72.75, 72.40, 52.38, 52.24, 47.75, 47.67, 37.93, 37.87, 36.44, 36.39, 31.67, 31.56. HRMS m/z (ESI) calculated for $C_{26}H_{25}BrO_4$ $(M + Na)^+$ 503.0828, found 503.0826.

Methyl 4-(4-(benzoyloxy)-1-methoxy-1-oxo-6-phenylhexan-2-yl)benzoate (33)



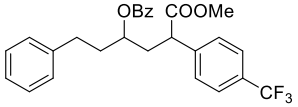
According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2e** (97.3 mg, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 10: 1) to afford 52.5 mg (57 % yield, 60:40 dr) of **33** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 7.5 Hz, 0.8H), 7.89 – 7.82 (m, 3H), 7.49 – 7.43 (m, 1H), 7.37 – 7.30 (m, 2H), 7.26 – 7.23 (m, 2H), 7.17 – 7.11 (m, 2H), 7.07 – 7.00 (m, 3H), 5.19 – 5.15 (m, 0.6H), 5.00 – 4.95 (m, 0.4H), 3.79 (s, 1.2H), 3.77 (s, 1.8H), 3.71 – 3.68 (m, 1H), 3.51 (s, 1.8H), 3.38 (s, 1.2H), 2.66 – 2.47 (m, 3H), 2.14 – 1.81 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.50, 173.16, 166.71, 166.65, 166.12, 165.98, 143.80, 143.50, 141.23, 141.08, 133.14, 133.01, 130.17, 130.11, 130.08, 129.69, 129.60, 129.49, 129.32, 128.50, 128.47, 128.46, 128.35, 128.34, 128.29, 128.12, 127.87, 126.05, 72.66, 72.37, 52.37, 52.23, 52.12, 52.08, 48.27, 48.16, 37.92, 37.75, 36.38, 31.63, 31.50. HRMS m/z (ESI) calculated for $C_{28}H_{28}O_6$ $(M + H)^+$ 461.1959 found 461.1959.

5-(4-Cyanophenyl)-6-methoxy-6-oxo-1-phenylhexan-3-yl benzoate (34)



According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2f** (77 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to afford 35.1 mg (41% yield, 57:43 dr) of **34** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 7.0 Hz, 0.9H), 7.83 (d, *J* = 7.0 Hz, 1.1H), 7.54 – 7.28 (m, 7H), 7.20 – 7.02 (m, 5H), 5.18 – 5.13 (m, 0.6H), 4.98 – 4.93 (m, 0.4H), 3.69 (t, *J* = 7.3 Hz, 1H), 3.55 (s, 1.7H), 3.42 (s, 1.3H), 2.68 – 2.44 (m, 3H), 2.15 – 1.82 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.15, 172.82, 166.17, 166.10, 143.93, 143.71, 141.17, 140.98, 133.38, 133.32, 132.71, 132.62, 129.98, 129.75, 129.62, 129.04, 128.81, 128.61, 128.59, 128.48, 128.41, 128.36, 118.66, 118.59, 111.71, 111.48, 72.60, 72.15, 52.63, 52.49, 48.52, 48.35, 37.87, 37.78, 36.49, 36.39, 31.67, 31.57. HRMS m/z (ESI) calculated for $C_{27}H_{25}NO_4$ $(M + H)^+$ 428.1856, found 428.1858.

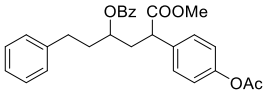
6-Methoxy-6-oxo-1-phenyl-5-(4-(trifluoromethyl)phenyl)hexan-3-yl benzoate (35)



According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2g** (89 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to afford 78.1 mg (83 % yield, 62:38 dr) of **35** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 7.5 Hz, 1.3H), 7.84 (d, *J* = 6.0 Hz,

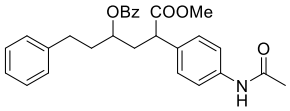
0.7H), 7.52 – 7.47 (m, 2H), 7.43 – 7.29 (m, 5H), 7.19 – 7.02 (m, 5H), 5.21 – 5.15 (m, 0.4H), 5.01 – 4.96 (m, 0.6H), 3.73 – 3.69 (m, 1H), 3.54 (s, 1.2H), 3.41 (s, 1.8H), 2.68 – 2.47 (m, 3H), 2.15 – 1.82 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.54, 173.21, 166.22, 166.13, 142.74, 142.50, 141.28, 141.10, 133.27, 133.17, 130.16, 129.77, 129.63, 128.57, 128.46 – 128.34 (m), 126.17, 125.95 – 125.75 (m), 124.17 (q, *J* = 273.5 Hz), 72.75, 72.38, 52.49, 52.35, 48.22, 48.20, 37.98, 37.93, 36.48, 36.42, 31.69, 31.59. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -62.55, -62.58. HRMS m/z (ESI) calculated for $C_{27}H_{25}F_3O_4$ $(M + H)^+$ 471.1778, found 471.1779.

5-(4-Acetoxyphenyl)-6-methoxy-6-oxo-1-phenylhexan-3-yl benzoate (36)



According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2h** (92 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 10: 1) to afford 66.3 mg (72% yield, 59:41 dr) of **36** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.97 – 7.91 (dd, *J* = 18.8 Hz, 6.8H, 2H), 7.51 – 7.47 (m, 1H), 7.40 – 7.35 (m, 2H), 7.22 – 7.14 (m, 4H), 7.08 – 7.03 (m, 3H), 6.96 – 6.92 (m, 2H) 5.19 – 5.14 (m, 0.6H), 5.06 – 5.01 (m, 0.4H), 3.67 – 3.61 (m, 1H), 3.52 (s, 1.8H), 3.37 (s, 1.2H), 2.68 – 2.49 (m, 3H), 2.20 (d, *J* = 4.5 Hz, 3H), 2.09 – 1.82 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 174.01, 173.64, 169.47, 169.45, 166.26, 166.12, 150.12, 150.03, 141.38, 141.26, 136.40, 136.05, 133.16, 133.08, 130.32, 130.23, 129.78, 129.70, 129.10, 128.87, 128.55, 128.52, 128.48, 128.40, 128.37, 126.09, 126.07, 121.98, 121.94, 72.80, 72.69, 52.33, 52.17, 47.83, 47.33, 38.26, 38.21, 36.53, 36.40, 31.71, 31.55, 21.24, 21.22. HRMS m/z (ESI) calculated for $C_{28}H_{28}O_6$ $(M + H)^+$ 461.1959, found 461.1955.

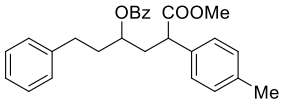
5-(4-Acetamidophenyl)-6-methoxy-6-oxo-1-phenylhexan-3-yl benzoate (37)



According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2i** (96.7 mg, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 5: 1) to afford 27.5 mg (30% yield, 62:38 dr) of **37** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (ddd, *J* = 18.0, 8.4, 1.4 Hz, 2H), 7.52 – 7.46 (m, 1H), 7.40 – 7.32 (m, 4H), 7.19 – 7.02 (m, 7H), 5.18 – 5.11 (m, 0.6H), 5.02 – 4.95 (m, 0.4H), 3.63 – 3.58 (m, 1H), 3.51 (s, 1.8H), 3.39 (s, 1.2H), 2.68 – 2.44 (m, 3H), 2.16 – 1.81 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.21, 173.86, 168.44, 166.30, 166.17, 141.40, 141.29, 137.48, 137.37, 134.61, 134.21, 133.17, 133.05, 130.35, 130.28,

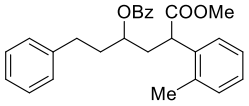
129.76, 129.71, 128.66, 128.56, 128.53, 128.45, 128.41, 128.37, 126.10, 126.08, 120.36, 120.33, 72.88, 72.67, 52.28, 52.16, 47.79, 47.47, 38.04, 37.90, 36.53, 35.96, 31.71, 31.57, 24.61. HRMS m/z (ESI) calculated for $C_{28}H_{29}NO_5$ $(M + H)^+$ 460.2118, found 460.2120.

6-Methoxy-6-oxo-1-phenyl-5-(p-tolyl)hexan-3-yl benzoate (38)



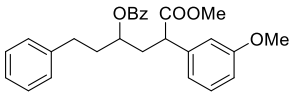
According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2j** (79 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 20: 1, then PE: DCM: = 3: 1) to afford 31.6 mg (38% yield, 60:40 dr) of **38** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 7.6 Hz, 0.8H), 7.90 (d, *J* = 7.6 Hz, 1.2H), 7.51 – 7.46 (m, 1H), 7.36 (q, *J* = 8.4 Hz, 2H), 7.19 – 6.98 (m, 9H), 5.19 – 5.13 (m, 0.6H), 5.01 – 4.95 (m, 0.4H), 3.63 – 3.58 (m, 1H), 3.51 (s, 1.8H), 3.39 (s, 1.2H), 2.68 – 2.46 (m, 3H), 2.21 (d, *J* = 8.6 Hz, 3H), 2.13 – 1.80 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.42, 174.03, 166.24, 166.10, 141.48, 141.37, 137.31, 137.20, 135.86, 135.47, 133.10, 133.00, 130.37, 130.33, 129.77, 129.71, 129.65, 129.58, 128.53, 128.50, 128.48, 128.40, 128.37, 127.92, 127.67, 126.05, 126.03, 72.94, 72.69, 52.24, 52.11, 47.91, 47.64, 38.13, 37.96, 36.54, 36.41, 31.69, 31.55, 21.18, 21.12. HRMS m/z (ESI) calculated for $C_{27}H_{28}O_4$ $(M + H)^+$ 417.2060, found 417.2062.

6-Methoxy-6-oxo-1-phenyl-5-(o-tolyl)hexan-3-yl benzoate (39)



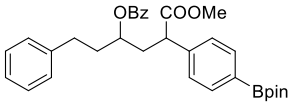
According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2k** (78 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to afford 53.3 mg (64% yield, 67:33 dr) of **39** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.96 – 7.92 (m, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.22 – 7.03 (m, 9H), 5.24 – 5.19 (m, 0.7H), 5.03 – 4.98 (m, 0.3H), 3.95 – 3.92 (m, 1H), 3.54 (s, 2H), 3.39 (s, 1H), 2.66 – 2.50 (m, 3H), 2.24 (s, 2H), 2.19 (s, 1H), 2.14 – 1.84 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.48, 174.21, 166.34, 166.12, 141.51, 141.34, 137.69, 137.01, 136.33, 135.70, 133.10, 133.06, 130.86, 130.82, 130.40, 129.76, 129.68, 128.54, 128.49, 128.47, 128.41, 128.40, 127.36, 127.28, 126.98, 126.74, 126.67, 126.65, 126.07, 73.33, 73.10, 52.23, 52.08, 43.63, 43.43, 37.98, 37.34, 36.61, 36.42, 31.74, 31.58, 19.80, 19.69. HRMS m/z (ESI) calculated for $C_{27}H_{28}O_4$ $(M + H)^+$ 417.2060, found 417.2063.

6-Methoxy-5-(3-methoxyphenyl)-6-oxo-1-phenylhexan-3-yl benzoate (42)



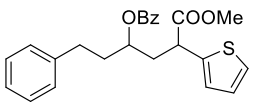
According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2n** (83 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 15: 1) to afford 52.7 mg (61% yield, 66:34 dr) of **42** as a yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ7.97 – 7.90 (m, 2H), 7.52 – 7.47 (m, 1H), 7.40 – 7.34 (q, *J* = 8.1 Hz, 2H), 7.20 – 7.03 (m, 6H), 6.79 – 6.65 (m, 3H), 5.21 – 5.16 (m, 0.7H), 5.05 – 4.99 (m, 0.3H), 3.68 – 3.59 (m, 4H), 3.53 (s, 2H), 3.41 (s, 1H), 2.69 – 2.47 (m, 3H), 2.14 – 1.82 (m, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 174.10, 173.74, 166.23, 166.08, 159.97, 159.94, 141.44, 141.33, 140.39, 140.01, 133.10, 133.01, 130.38, 130.34, 129.90, 129.85, 129.76, 129.70, 128.53, 128.50, 128.41, 128.40, 128.36, 126.06, 126.04, 120.34, 120.14, 113.66, 113.59, 113.22, 112.90, 72.93, 72.71, 55.28, 55.26, 52.27, 52.13, 48.39, 48.07, 38.12, 37.96, 36.52, 36.43, 31.70, 31.55. HRMS m/z (ESI) calculated for $C_{27}H_{28}O_5$ $(M + H)^+$ 433.2010, found 433.2006.

6-Methoxy-6-oxo-1-phenyl-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)hexan-3-yl benzoate (43)



According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2o** (141 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 15: 1) to afford 81.2 mg (77 % yield, 62:38 dr) of **43** as a yellow oil. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.02 (d, *J* = 7.0 Hz, 0.8H), 7.97 (d, *J* = 7.0 Hz, 1.2H), 7.74 (q, *J* = 14.8 Hz, 2H), 7.56 (q, *J* = 7.7 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.29 – 7.21 (m, 4H), 7.17 – 7.09 (m, 3H), 5.28 – 5.23 (m, 0.6H), 5.08 – 5.03 (m, 0.4H), 3.75 – 3.71(m, 1H), 3.59 (s, 1.8H), 3.46 (s, 1.2H), 2.75 – 2.56 (m, 3H), 2.22 – 1.90 (m, 3H), 1.33 (d, *J* = 4.8 Hz, 12H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 174.03, 173.66, 166.28, 166.09, 142.00, 141.59, 141.44, 141.33, 135.46, 135.41, 133.13, 133.05, 130.32, 129.78, 129.72, 128.55, 128.52, 128.50, 128.42, 128.38, 127.48, 127.23, 126.08, 126.05, 83.92, 83.90, 72.91, 72.69, 52.33, 52.19, 48.53, 48.23, 38.05, 37.81, 36.52, 36.45, 31.72, 31.56, 24.99, 24.96. HRMS m/z (ESI) calculated for $C_{32}H_{37}BO_6$ $(M + H)^+$ 529.2756, found 529.2758.

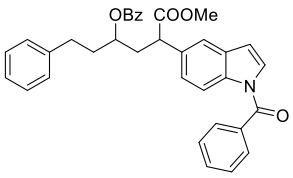
6-Methoxy-6-oxo-1-phenyl-5-(thiophen-2-yl)hexan-3-yl benzoate (44)



According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2p** (63 μL, 0.6 mmol). The crude product

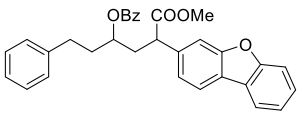
was purified by flash column chromatography on silica gel (PE: EA = 10: 1) to afford 35.2 mg (43% yield, 55:45 dr) of **44** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.03 (qd, *J* = 7.3, 1.5 Hz, 2H), 7.59 – 7.55 (m, 1H), δ 7.45 (q, *J* = 7.3 Hz, 2H), 7.27 – 7.11 (m, 6H), 6.93 – 6.89 (m, 2H), 5.28 – 5.23 (m, 0.4H), 5.17 – 5.12 (m, 0.6H), 4.07 – 4.02 (m, 1H), 3.63 (s, 1.3H), 3.52 (s, 1.7H), 2.76 – 2.58 (m, 3H), 2.26 – 2.20 (m, 1H), 2.13 – 1.92 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.35, 172.94, 166.23, 166.10, 141.34, 141.27, 141.07, 140.49, 133.18, 133.12, 130.28, 130.24, 129.79, 129.74, 128.57, 128.54, 128.52, 128.48, 128.41, 128.38, 126.96, 126.91, 126.14, 126.11, 126.09, 125.46, 125.11, 124.80, 72.53, 72.47, 52.52, 52.41, 43.82, 43.18, 39.10, 38.99, 36.49, 36.30, 31.71, 31.53. HRMS m/z (ESI) calculated for $C_{24}H_{24}O_4S$ $(M + H)^+$ 409.1468, found 409.1473.

5-(1-Benzoyl-1*H*-indol-5-yl)-6-methoxy-6-oxo-1-phenylhexan-3-yl benzoate (45)



According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2q** (148.3 mg, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 8: 1) to afford 52.3 mg (48% yield, 59:41 dr) of **45** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.23 (d, *J* = 8.8 Hz, 0.4H), 8.18 (d, *J* = 8.4 Hz, 0.6H), 7.95 (d, *J* = 6.8 Hz, 0.8H), 7.87 (d, *J* = 8.0 Hz, 1.2H), 7.63 – 7.59 (m, 2H), 7.52 – 7.29 (m, 7H), 7.22 – 7.01 (m, 7H), 6.45 (dd, *J* = 9.4, 3.8 Hz, 1H), 5.24 – 5.18 (m, 0.6H), 5.05 – 4.99 (m, 0.4H), 3.79 – 3.74 (m, 1H), 3.53 (s, 1.8H), 3.41 (s, 1.2H), 2.66 – 2.53 (m, 3H), 2.24 – 2.11 (m, 1H), 2.06 – 1.82 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.45, 174.09, 168.61, 168.54, 166.22, 166.10, 141.45, 141.32, 135.48, 135.35, 134.60, 134.53, 134.50, 134.20, 133.09, 132.93, 132.04, 131.33, 131.28, 130.31, 130.27, 129.75, 129.63, 129.23, 129.21, 128.71, 128.53, 128.49, 128.46, 128.40, 128.36, 128.31, 128.21, 128.17, 126.05, 126.03, 124.92, 124.75, 120.33, 120.02, 116.81, 116.75, 108.63, 108.54, 72.96, 72.71, 52.29, 52.16, 48.22, 48.12, 38.40, 38.15, 36.52, 36.49, 31.69, 31.57. HRMS m/z (ESI) calculated for $C_{35}H_{31}NO_5$ $(M + H)^+$ 546.2275, found 546.2277.

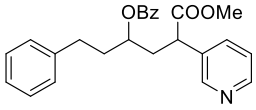
5-(Dibenzo[*b*,*d*]furan-3-yl)-6-methoxy-6-oxo-1-phenylhexan-3-yl benzoate (46)



According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2r** (116.4 mg, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 15: 1) to afford 74.8 mg (76% yield, 62:38 dr) of **46** as a yellow

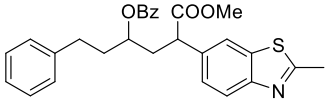
oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.96 – 7.93 (m, 0.7H), 7.85 – 7.70 (m, 3.3H), 7.47 – 6.99 (m, 13H), 5.24 – 5.18 (m, 0.6H), 5.06 – 5.00 (m, 0.4H), 3.82 – 3.78 (m, 1H), 3.53 (s, 1.9H), 3.41 (s, 1.1H), 2.69 – 2.53 (m, 3H), 2.24 – 2.13 (m, 1H), 2.06 – 1.82 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.07, 173.73, 166.23, 166.12, 156.62, 156.58, 156.52, 141.40, 141.24, 138.27, 137.96, 133.11, 132.91, 130.28, 130.20, 129.76, 129.60, 128.55, 128.50, 128.48, 128.41, 128.36, 128.30, 127.28, 127.22, 126.09, 126.06, 124.04, 123.99, 123.82, 123.66, 122.95, 122.88, 122.82, 122.65, 120.96, 120.89, 120.72, 120.66, 111.77, 111.73, 111.25, 111.12, 72.91, 72.64, 52.38, 52.25, 48.60, 48.54, 38.36, 38.24, 36.52, 31.71, 31.60. HRMS m/z (ESI) calculated for $C_{32}H_{28}O_5$ $(M + H)^+$ 493.2010, found 493.2012.

6-Methoxy-6-oxo-1-phenyl-5-(pyridin-3-yl)hexan-3-yl benzoate (47)



According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2s** (64 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 2: 1) to afford 50.3 mg (62% yield, 62:38 dr) of **47** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.52 – 8.44 (m, 2H), 8.02 (d, *J* = 7.0 Hz, 0.9H), 7.97 (d, *J* = 7.0 Hz, 1.3H), 7.65 – 7.55 (m, 2H), 7.47 – 7.42 (m, 2H), 7.27 – 7.11 (m, 6H), 5.28 – 5.23 (m, 0.6H), 5.12 – 5.07 (m, 0.4H), 3.78 – 3.72 (m, 1H), 3.61 (s, 1.8H), 3.48 (s, 1.2H), 2.76 – 2.57 (m, 3H), 2.21 – 1.92 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.39, 173.05, 166.16, 166.02, 149.41, 149.24, 148.81, 148.66, 141.17, 141.04, 135.65, 135.32, 134.60, 134.31, 133.22, 133.14, 130.09, 130.03, 129.73, 129.65, 128.55, 128.53, 128.51, 128.45, 128.35, 128.32, 126.12, 123.77, 72.59, 72.31, 52.46, 52.33, 45.92, 45.64, 37.86, 37.76, 36.37, 36.33, 31.66, 31.54. HRMS m/z (ESI) calculated for $C_{25}H_{25}NO_4$ $(M + H)^+$ 404.1856, found 404.1856.

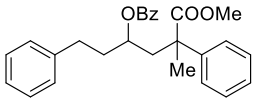
6-Methoxy-5-(2-methylbenzo[d]thiazol-6-yl)-6-oxo-1-phenylhexan-3-yl benzoate (48)



According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2t** (89 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 2: 1) to afford 56.8 mg (60% yield, 60:40 dr) of **48** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.02 (d, *J* = 7.3 Hz, 0.8H), 7.92 (d, *J* = 7.3 Hz, 1.2H), 7.84 (dd, *J* = 16.2, 8.4 Hz, 1H), 7.72 (s, 1H), 7.58 – 7.32 (m, 4H), 7.26 – 7.08 (m, 5H), 5.31 – 5.25 (m, 0.6H), 5.13 – 5.07 (m, 0.4H), 3.86 – 3.81 (m, 1H),

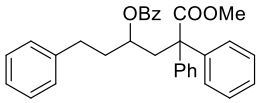
3.61 (s, 1.8H), 3.48 (s, 1.2H), 2.79 (d, *J* = 10.2 Hz, 3H), 2.75 – 2.59 (m, 3H), 2.29 – 1.90 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.05, 173.70, 167.36, 167.26, 166.17, 166.06, 152.90, 152.76, 141.31, 141.14, 136.30, 136.25, 135.53, 135.21, 133.12, 132.96, 130.16, 130.09, 129.70, 129.55, 128.51, 128.47, 128.36, 128.31, 126.09, 126.06, 125.89, 122.66, 122.58, 120.81, 120.58, 72.81, 72.54, 52.36, 52.21, 48.14, 48.09, 38.31, 38.16, 36.47, 36.41, 31.64, 31.54, 20.18, 20.14. HRMS m/z (ESI) calculated for $C_{28}H_{27}NO_4S$ $(M + H)^+$ 474.1734, found 474.1736.

6-Methoxy-5-methyl-6-oxo-1,5-diphenylhexan-3-yl benzoate (49)



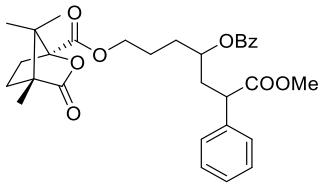
According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2u** (70.9 mg, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to afford 39.0 mg (47% yield, 56:44 dr) of **49** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 6.8 Hz, 0.8H), 7.69 (d, *J* = 8.8 Hz, 1.2H), 7.50 – 6.94 (m, 13H), 5.31 – 5.25 (m, 0.6H), 5.21 – 5.14 (m, 0.4H), 3.56 (s, 1.7H), 3.40 (s, 1.3H), 2.68 – 2.20 (m, 4H), 1.98 – 1.72 (m, 2H), 1.56 (d, *J* = 4.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.53, 176.40, 166.01, 165.92, 143.28, 141.58, 141.47, 133.06, 132.84, 130.45, 130.30, 129.79, 129.64, 128.72, 128.56, 128.51, 128.50, 128.42, 128.39, 128.18, 127.15, 126.83, 126.05, 126.02, 125.82, 71.86, 71.49, 52.48, 52.34, 49.47, 48.89, 43.85, 43.53, 37.78, 37.61, 31.46, 31.41, 22.30, 21.94. HRMS m/z (ESI) calculated for $C_{27}H_{28}O_4$ $(M + H)^+$ 417.2060, found 417.2058.

6-Methoxy-6-oxo-1,5,5-triphenylhexan-3-yl benzoate (50)



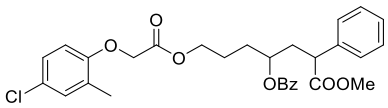
According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2v** (108.1 mg, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 15: 1) to afford 74.6 mg (78% yield) of **50** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.69 (d, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1.1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.22 – 7.01 (m, 14H), 6.95 (t, *J* = 7.5 Hz, 1H), 5.00 – 4.95 (m, 1H), 3.54 (s, 3H), 2.94 (q, *J* = 7.5 Hz, 1H), 2.75 (dd, *J* = 14.5, 3.5 Hz, 1H), 2.55 (t, *J* = 8.3 Hz, 2H), 1.92 – 1.78 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 174.42, 165.58, 142.67, 142.63, 141.71, 132.71, 130.48, 129.63, 129.08, 128.82, 128.45, 128.40, 128.16, 128.09, 128.07, 127.11, 127.03, 125.93, 72.06, 52.61, 42.63, 37.53, 31.26. HRMS m/z (ESI) calculated for $C_{32}H_{30}O_4$ $(M + H)^+$ 479.2217, found 479.2218.

4-(Benzoyloxy)-7-methoxy-7-oxo-6-phenylheptyl (1*S*,4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (51)



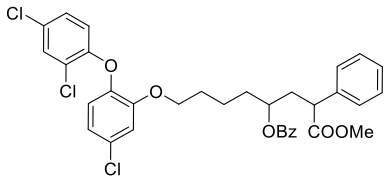
According to general procedure, the reaction was carried out with **1aa** (53.6 mg, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 5: 1) to afford 36.5 mg (34% yield, 60:40 dr) of **51** as a yellow oil. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.01 (dd, *J* = 26.3, 7.7 Hz, 2H), 7.58 (q, *J* = 7.3 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.32– 7.20 (m, 5H), 5.24 – 5.21 (m, 0.6H), 5.06 – 5.03 (m, 0.4H), 4.24 – 4.18 (m, 2H), 3.73 – 3.68 (m, 1H), 3.62 (s, 1.8H), 3.48 (s, 1.2H), 2.63 – 2.51 (m, 1H), 2.43 – 2.34 (m, 1H), 2.17 – 1.67 (m, 9H), 1.10 (s, 3H), 1.03 – 1.01 (m, 3H), 0.93 (dd, *J* = 10.8, 6.5 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 178.18, 178.16, 174.10, 173.75, 167.52, 167.49, 166.19, 166.01, 138.73, 138.31, 133.25, 133.16, 130.11, 130.04, 129.75, 129.68, 128.96, 128.91, 128.54, 128.47, 128.01, 127.75, 127.70, 127.55, 91.17, 91.15, 72.45, 72.15, 65.20, 65.18, 64.65, 54.84, 54.19, 54.18, 52.29, 52.15, 48.98, 47.97, 38.14, 37.92, 31.20, 31.06, 30.72, 29.02, 24.55, 24.53, 24.39, 16.84, 16.82, 9.79. HRMS m/z (ESI) calculated for $C_{31}H_{36}O_8$ $(M + H)^+$ 537.2483, found 537.2486.

7-(2-(4-Chloro-2-methylphenoxy)acetoxy)-1-methoxy-1-oxo-2-phenylheptan-4-yl benzoate (52)



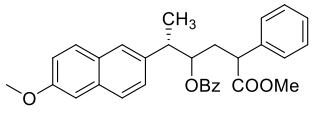
According to general procedure, the reaction was carried out with **1ab** (54.0 mg, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 8: 1) to afford 54.9 mg (51% yield, 61:39 dr) of **52** as a yellow oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.01 (ddd, *J* = 20.8, 8.3, 1.4 Hz, 2H), 7.60 – 7.55 (m, 1H), 7.48 – 7.42 (m, 2H), 7.33 – 7.20 (m, 5H), 7.11 – 7.03 (m, 2H), 6.59 (t, *J* = 8.9 Hz, 1H), 5.23 – 5.19 (m, 0.6H), 5.04 – 5.01 (m, 0.4H), 4.58 (d, *J* = 14.8 Hz, 2H), 4.21 – 4.14 (m, 2H), 3.72 – 3.66 (m, 1H), 3.61 (s, 1.8H), 3.48 (s, 1.2H), 2.61 – 2.48 (m, 1H), 2.23 (d, *J* = 4.4 Hz, 3H), 2.14 – 2.02 (m, 1H), 1.76 – 1.67 (m, 4H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 174.12, 173.78, 168.86, 168.82, 166.20, 166.02, 154.77, 154.75, 138.79, 138.35, 133.26, 133.16, 130.88, 130.15, 130.08, 129.75, 129.68, 129.31, 128.97, 128.92, 128.55, 128.49, 128.02, 127.75, 127.71, 127.56, 126.41, 126.23, 112.29, 73.64, 72.48, 72.19, 65.76, 65.73, 64.94, 64.90, 52.29, 52.15, 48.33, 47.96, 39.70, 37.94, 31.24, 31.14, 24.48, 24.33, 15.73. HRMS m/z (ESI) calculated for $C_{30}H_{31}ClO_7$ $(M + H)^+$ 539.1831, found 539.1841.

8-(5-Chloro-2-(2,4-dichlorophenoxy)phenoxy)-1-methoxy-1-oxo-2-phenyloctan-4-yl benzoate (53)



According to general procedure, the reaction was carried out with **1ac** (74.4 mg, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 10: 1) to afford 61.5 mg (48% yield, 59:41 dr) of **53** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03 – 7.96 (m, 2H), 7.58 – 7.53 (m, 1H), 7.46 – 7.40 (m, 2H), 7.36 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.29 – 7.18 (m, 5H), 7.05 (dt, *J* = 8.8, 2.0 Hz, 1H), 6.92 – 6.87 (m, 3H), 6.60 (dd, *J* = 8.9, 2.1 Hz, 1H), 5.18 – 5.12 (m, 0.6H), 5.00 – 4.94 (m, 0.4H), 3.90 – 3.83 (m, 2H), 3.74 – 3.67 (m, 1H), 3.60 (s, 1.8H), 3.46 (s, 1.2H), 2.59 – 2.48 (m, 1H), 2.14 – 2.01 (m, 1H), 1.85 – 1.52 (m, 4H), 1.44 – 1.25 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.21, 173.84, 166.20, 166.04, 152.56, 150.97, 150.94, 143.18, 143.15, 138.93, 138.52, 133.09, 132.99, 130.58, 130.19, 129.74, 129.67, 128.92, 128.87, 128.47, 128.40, 128.04, 127.87, 127.85, 127.80, 127.64, 127.48, 124.53, 122.07, 122.04, 121.01, 118.07, 118.03, 114.87, 114.83, 72.88, 72.73, 68.93, 68.88, 52.24, 52.09, 48.43, 48.00, 37.99, 37.82, 34.36, 34.13, 28.77, 21.53, 21.44. HRMS m/z (ESI) calculated for $C_{34}H_{31}Cl_3O_6$ $(M + Na)^+$ 663.1078, found 663.1087.

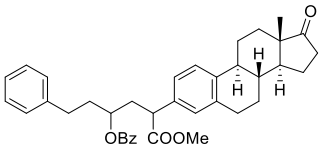
(2*S*)-6-Methoxy-2-(6-methoxynaphthalen-2-yl)-6-oxo-5-phenylhexan-3-yl benzoate (54)



According to general procedure, the reaction was carried out with **1ad** (43.0 mg, 0.2 mmol), **2a** (69 μL, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 15: 1) to afford 31.8 mg (33% yield, 60:40 dr) of **54** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.09 – 7.92 (m, 2H), 7.70 – 7.62 (m, 2H), 7.60 – 7.49 (m, 2H), 7.48 – 7.33 (m, 3H), 7.23 – 7.08 (m, 7H), 5.55 – 5.50 (m, 0.6H), 5.33 – 5.27(m, 0.4H), 3.90 (dd, *J* = 4.5, 2.8 Hz, 3H), 3.67 – 3.56 (m, 3H), 3.37 – 3.16 (m, 2H), 2.53 – 2.35 (m, 1H), 2.11 – 1.84 (m, 1H), 1.42 – 1.29 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.22, 173.81, 173.70, 166.32, 166.28, 166.09, 157.57, 157.53, 139.03, 138.94, 138.24, 138.17, 137.90, 137.84, 137.33, 136.99, 133.66, 133.60, 133.19, 133.12, 133.07, 132.98, 130.31, 130.26, 129.88, 129.78, 129.69, 129.33, 129.29, 129.27, 129.08, 129.00, 128.98, 128.96, 128.79, 128.74, 128.56, 128.52, 128.46, 128.41, 128.19, 128.10, 127.83, 127.77, 127.75, 127.54, 127.38, 127.32, 127.30, 127.19, 127.16, 126.85, 126.80, 126.77, 126.59, 126.55, 126.40, 118.96, 118.86,

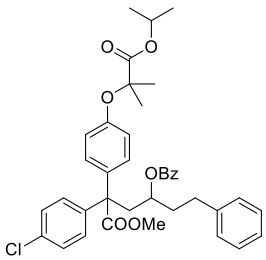
105.68, 105.64, 76.79, 76.51, 76.43, 55.38, 52.19, 52.16, 51.98, 51.95, 48.51, 48.44, 48.18, 48.02, 44.73, 44.22, 43.75, 43.25, 36.15, 36.02, 35.97, 34.61, 18.26, 18.06, 17.23, 15.69. HRMS m/z (ESI) calculated for $C_{31}H_{30}O_5$ $(M + H)^+$ 483.2166, found 483.2163.

6-Methoxy-5-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)-6-oxo-1-phenylhexan-3-yl benzoate (55)



According to general Procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2w** (168.1 mg, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 5: 1) to afford 61.5 mg (53 % yield, 61:39 dr) of **55** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.03 (d, *J* = 8.3 Hz, 0.8H), 7.97 – 7.94 (m, 1.2H), 7.59 – 7.53 (m, 1H), 7.44 (dt, *J* = 15.5, 7.6 Hz, 2H), 7.26 – 6.97 (m, 8H), 5.29 – 5.24 (m, 0.6H), 5.12 – 5.05 (m, 0.4H), 3.69 – 3.64 (m, 1H), 3.60 (d, *J* = 0.8 Hz, 1.8H), 3.48 (d, *J* = 1.1 Hz, 1.2H), 2.87 – 2.79 (m, 2H), 2.72 – 2.61 (m, 2H), 2.59 – 2.46 (m, 2H), 2.41 – 2.34 (m, 1H), 2.28 – 1.93 (m, 8H), 1.64 – 1.27 (m, 6H), 0.90 – 0.88 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.35, 174.01, 173.99, 166.13, 166.05, 141.44, 141.34, 139.08, 139.06, 138.94, 137.04, 137.01, 136.96, 136.22, 135.86, 133.07, 132.93, 130.35, 130.33, 130.31, 129.73, 129.65, 128.55, 128.50, 128.47, 128.45, 128.40, 128.37, 128.34, 126.03, 126.01, 125.90, 125.85, 125.83, 125.39, 125.31, 125.12, 125.08, 72.94, 72.77, 72.75, 52.23, 52.09, 50.60, 50.58, 48.04, 48.02, 47.82, 47.75, 47.72, 44.38, 44.33, 38.10, 38.06, 37.87, 36.52, 36.41, 35.92, 31.66, 31.63, 31.49, 29.39, 29.35, 26.50, 25.64, 21.65, 13.94. HRMS m/z (ESI) calculated for $C_{38}H_{42}O_5$ $(M + H)^+$ 579.3105, found 579.3114.

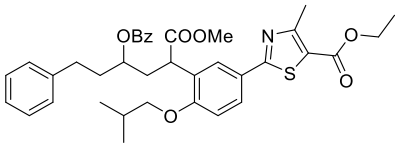
5-(4-Chlorophenyl)-5-(4-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)phenyl)-6-methoxy-6-oxo-1-phenylhexan-3-yl benzoate (56)



According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2x** (214.9 mg, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 20: 1) to afford 81.3 mg (62% yield, 55:45 dr) of **56** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.77 (dd, *J* = 50.2, 7.7 Hz, 2H), 7.50 (dd, *J* = 10.2, 7.4 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.25 – 7.21 (m, 3H), 7.16 – 7.07 (m, 7H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.71 (dd, *J* = 16.1, 8.5 Hz, 2H), 5.09– 5.03 (m, 1.5H), 4.99 – 4.95 (m, 0.5H), 3.62 (s, 1.5H), 3.57

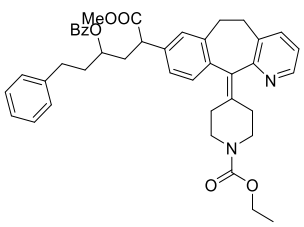
(s, 1.5H), 3.09 – 3.04 (m, 0.5H), 2.87 – 2.77 (m, 1H), 2.67 – 2.59 (m, 2.5H), 2.00 – 1.86 (m, 1H), 1.54 (dd, *J* = 27.2, 2.9 Hz, 6H), 1.20 – 1.18 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.15, 174.05, 173.63, 165.56, 165.53, 154.82, 141.61, 141.51, 141.42, 141.17, 135.52, 135.03, 132.94, 132.91, 132.82, 130.57, 130.28, 130.20, 130.16, 129.56, 129.41, 129.35, 128.47, 128.38, 128.36, 128.28, 128.18, 128.16, 128.11, 125.99, 125.97, 118.16, 72.05, 71.61, 69.02, 69.00, 58.10, 57.88, 52.66, 42.69, 42.45, 37.56, 37.39, 31.23, 31.21, 25.55, 25.51, 25.50, 25.35, 21.64. HRMS m/z (ESI) calculated for $C_{39}H_{41}ClO_7$ $(M + Na)^+$ 679.2433, found 679.2435.

Ethyl 2-(3-(4-(benzoyloxy)-1-methoxy-1-oxo-6-phenylhexan-2-yl)-4-isobutoxyph enyl)-4-methylthiazole-5-carboxylate (57)



According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2y** (207.1 mg, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 5: 1) to afford 56.6 mg (44 % yield, 53:47 dr) of **57** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 – 7.85 (m, 2H), 7.77 – 7.65 (m, 2H), 7.50 – 7.42 (m, 1H), 7.37 – 7.28 (m, 2H), 7.18 – 7.02 (m, 5H), 6.74 (dd, *J* = 22.4, 8.6 Hz, 1H), 5.29 – 5.23 (m, 0.5H), 4.98 – 4.91 (m, 0.5H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.07 (ddd, *J* = 33.1, 8.9, 5.6 Hz, 1H), 3.65 – 3.59 (m, 2H), 3.55 (s, 1.6H), 3.47 (s, 1.4H), 2.67 – 2.51 (m, 6H), 2.29 – 1.79 (m, 4H), 1.31 (td, *J* = 7.1, 1.1 Hz, 3H), 0.89 – 0.85 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.98, 173.83, 169.71, 169.70, 166.22, 165.96, 162.54, 162.52, 161.10, 158.80, 158.49, 141.54, 141.40, 132.99, 132.89, 130.40, 130.35, 129.76, 129.71, 128.69, 128.49, 128.46, 128.43, 128.39, 128.34, 128.25, 127.72, 127.51, 127.44, 127.31, 126.01, 125.98, 125.79, 125.77, 120.88, 111.70, 111.68, 74.87, 74.84, 73.37, 72.63, 61.21, 61.17, 52.25, 52.14, 42.45, 41.68, 36.93, 36.67, 36.41, 35.74, 31.71, 31.56, 28.36, 28.27, 19.35, 19.33, 19.26, 19.21, 17.64, 14.48. HRMS m/z (ESI) calculated for $C_{37}H_{41}NO_7S$ $(M + H)^+$ 644.2676, found 644.2678.

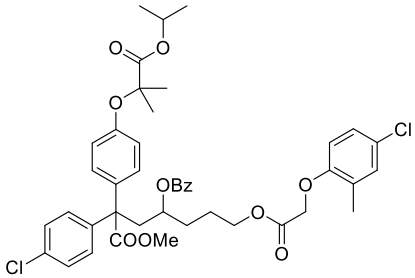
Ethyl 4-(8-(4-(benzoyloxy)-1-methoxy-1-oxo-6-phenylhexan-2-yl)-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate (58)



According to general procedure, the reaction was carried out with **1a** (27 μL, 0.2 mmol), **2z** (224.5 mg, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 1: 1) to afford 65.9 mg (49 % yield,

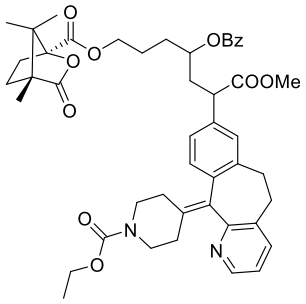
61:39 dr) of **58** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.40 (s, 1H), 8.05 – 7.94 (m, 2H), 7.58 – 7.49 (m, 1H), 7.46 – 7.36 (m, 3H), 7.25 – 7.04 (m, 9H), 5.29 – 5.22 (m, 0.6H), 5.12 – 5.07 (m, 0.4H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 2H), 3.71 – 3.64 (m, 1.2H), 3.59 (s, 1.8H), 3.45 (d, *J* = 5.8 Hz, 1.2H), 3.38 – 3.25 (m, 2H), 3.17 – 3.10 (m, 2H), 2.85 – 2.55 (m, 5H), 2.47 (s, 1H), 2.35 – 2.29 (m, 3H), 2.17 – 1.90 (m, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.18, 174.14, 173.85, 173.80, 166.17, 166.02, 157.63, 155.56, 146.61, 141.34, 141.32, 141.20, 138.30, 138.22, 138.13, 138.09, 137.89, 137.87, 137.54, 137.46, 137.40, 137.35, 136.96, 134.93, 133.78, 133.09, 133.07, 133.00, 132.98, 130.29, 130.24, 130.21, 129.91, 129.88, 129.83, 129.81, 129.68, 129.61, 129.57, 128.89, 128.71, 128.46, 128.44, 128.42, 128.39, 128.32, 128.29, 128.28, 126.00, 125.97, 125.54, 125.41, 125.36, 122.21, 72.89, 72.81, 72.75, 72.65, 61.32, 52.24, 52.08, 48.03, 48.00, 47.69, 47.55, 44.95, 44.85, 38.14, 37.99, 37.93, 36.44, 36.37, 36.33, 31.97, 31.66, 31.62, 31.57, 31.43, 30.77, 30.58, 14.76. HRMS m/z (ESI) calculated for $C_{42}H_{44}N_2O_6$ $(M + H)^+$ 673.3272, found 673.3272.

7-(2-(4-Chloro-2-methylphenoxy)acetoxy)-2-(4-chlorophenyl)-2-(4-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)phenyl)-1-methoxy-1-oxoheptan-4-yl benzoate (59)



According to general procedure, the reaction was carried out with **1ab** (54.0 mg, 0.2 mmol), **2x** (214.9 mg, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 7: 1) to afford 57 mg (36% yield, 53:47 dr) of **59** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.66 (dd, *J* = 51.5, 7.7 Hz, 2H), 7.46 – 7.41 (m, 1H), 7.29 (dt, *J* = 15.4, 7.6 Hz, 2H), 7.09 – 6.92 (m, 8H), 6.64 (dd, *J* = 22.5, 8.4 Hz, 2H), 6.51 (dd, *J* = 8.8, 5.5 Hz, 1H), 5.01 – 4.83 (m, 2H), 4.49 (d, *J* = 9.3 Hz, 2H), 4.06 (dt, *J* = 17.1, 6.0 Hz, 2H), 3.53 (d, *J* = 27.0 Hz, 3H), 2.93 – 2.50 (m, 2H), 2.16 (s, 3H), 1.65 – 1.41 (m, 10H), 1.12 (t, *J* = 6.4 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.12, 174.03, 173.59, 168.87, 168.83, 165.47, 165.44, 154.86, 154.82, 154.78, 141.35, 141.13, 135.45, 134.82, 133.02, 132.98, 132.93, 130.86, 130.52, 130.18, 130.05, 129.91, 129.53, 129.37, 129.32, 128.32, 128.20, 128.17, 128.14, 126.41, 126.21, 118.17, 112.32, 79.16, 79.03, 71.47, 71.08, 69.03, 69.00, 65.75, 65.02, 64.98, 58.14, 57.91, 52.69, 42.66, 42.35, 32.31, 32.11, 25.49, 25.31, 24.09, 24.05, 21.63, 16.22. HRMS m/z (ESI) calculated for $C_{43}H_{46}Cl_2O_{10}$ $(M + Na)^+$ 815.2360, found 815.2377.

Ethyl 4-(8-(4-(benzoyloxy)-1-methoxy-1-oxo-7-(((1*S*,4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carbonyl)oxy)heptan-2-yl)-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate (60)

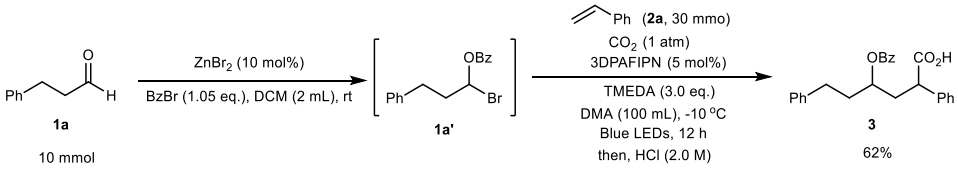


According to general procedure, the reaction was carried out with **1aa** (53.6 mg, 0.2 mmol), **2z** (224.5 mg, 0.6 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 2: 1) to afford 67.7 mg (42 % yield, 58:42 dr) of **60** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.39 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.04 – 7.92 (m, 2H), 7.60 – 7.36 (m, 4H), 7.14 – 7.03 (m, 4H), 5.25 – 5.20 (m, 0.6H), 5.11 – 5.05 (m, 0.4H), 4.24 – 4.11 (m, 4H), 3.79 (s, 2H), 3.68 – 3.61 (m, 3H), 3.45 (d, *J* = 6.1 Hz, 1H), 3.41 – 3.26 (m, 2H), 3.19 – 3.09 (m, 2H), 2.88 – 2.71 (m, 2H), 2.64 – 2.26 (m, 6H), 2.12 – 1.96 (m, 2H), 1.91 – 1.87 (m, 1H), 1.78 – 1.63 (m, 5H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.10 (d, *J* = 2.4 Hz, 3H), 1.01 (dd, *J* = 7.6, 3.1 Hz, 3H), 0.94 – 0.90 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.13, 174.03, 173.72, 173.67, 167.43, 166.11, 165.93, 157.50, 155.52, 146.47, 138.09, 137.71, 137.41, 137.02, 136.97, 134.74, 133.79, 133.19, 133.09, 129.98, 129.93, 129.90, 129.86, 129.80, 129.63, 129.55, 129.51, 128.83, 128.66, 128.48, 128.44, 128.41, 128.38, 128.34, 125.47, 125.31, 122.22, 91.10, 91.07, 72.39, 72.33, 72.16, 65.11, 61.29, 54.75, 54.11, 52.24, 52.07, 47.99, 47.95, 47.63, 47.49, 44.89, 44.78, 38.15, 37.83, 31.90, 31.56, 31.48, 31.08, 31.02, 30.63, 28.92, 24.42, 24.28, 16.76, 16.73, 14.70, 9.70. HRMS m/z (ESI) calculated for $C_{47}H_{54}N_2O_{10}$ $(M + H)^+$ 807.3851, found 807.3849.

6. Synthetic applications

6.1 Continuous-flow reaction

Figure S2. The device of continuous-flow reaction

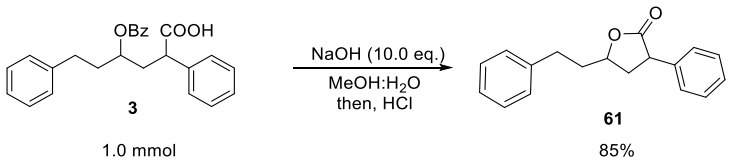


In glovebox, an oven-dried 8.0 mL vial with a stirring bar was added with $ZnBr_2$ (225.2 mg, 1.0 mmol, 10 mol%), followed by the addition of DCM (2.0 mL) and benzoyl bromide (1.24 mL, 10.5 mmol, 1.05 eq.). The mixture was stirred for 10 min at room temperature. To the mixture **1a** (1.32 mL, 10.0 mmol, 1.0 eq.) was added and the resulting mixture was stirred for 2 h at room temperature. After reaction completed, the mixture was filtered through a pad of neutral Al_2O_3 and the solvent was removed in vacuo to afford **1a'** without further purification. The flow photoredox system was evacuated and back-filled with CO_2 for 3 times and the reaction bottle was charged with **1a'**, 3DPAFIPN (324 mg, 0.5 mmol, 5 mol%), DMA (100.0 mL), **2a** (3.46 mL, 30.0 mmol, 3.0 eq.) and TMEDA (4.5 mL, 30.0 mmol, 3.0 eq.) under CO_2 atmosphere. The

bottle was cooled down to –10 °C and a CO_2 balloon was put into the bottle. The mixture solution pumped via peristatic pump to pass through the flow photoredox system with a flow rate of 3 mL/min (reaction mixture) and 10 mL/min (CO_2) at –10 °C under blue LEDs (455 nm, 15W) irradiation. After 4.8 h, the outlet solution was collected and diluted with EA. The resulting mixture was quenched by 2.0 mL of 2 M HCl (aq.). After stirring for 15 min at room temperature, the mixture was extracted with EA, the combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (PE: EA: CH_3COOH = 2: 1: 0.5%) to afford 2.41 g (62 % yield, 61:39 dr) of **3** as a yellow oil.

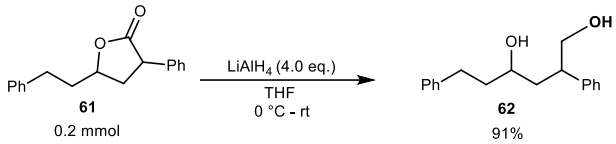
6.2 Divergent transformation

5-Phenethyl-3-phenyldihydrofuran-2(3*H*)-one (61)



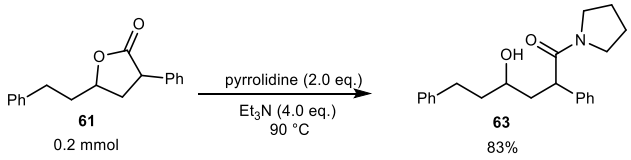
To a solution of **3** (388.2 mg, 1.0 mmol, 1.0 eq.) in MeOH (10.0 mL, 0.1M), H_2O (10.0 mL, 0.1M) and NaOH (400.0 mg, 10.0 mmol, 10.0 eq.) were added at room temperature. After stirring for 3 h at 70 °C, the mixture was acidified with 2 M HCl (to pH = 1). The reaction mixture was stirred at room temperature for another 3 h. After completion, the MeOH was removed under reduced pressure, the aqueous layer was extracted with EA. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (DCM) to afford 226.2 mg (85 % yield, 61:39 dr) of **61** as a white solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.35 – 7.22 (m, 10H), 4.65 – 4.59 (m, 0.6H), 4.48 – 4.42 (m, 0.4H), 3.88 (dt, *J* = 33.3, 9.7 Hz, 1H), 2.89 – 1.93 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.22, 176.83, 140.75, 137.16, 136.60, 129.08, 128.93, 128.67, 128.56, 128.55, 128.17, 127.71, 127.68, 126.33, 78.03, 77.61, 47.31, 45.68, 38.09, 37.39, 37.23, 36.41, 31.83, 31.74. HRMS m/z (ESI) calculated for $C_{18}H_{18}O_2$ $(M + H)^+$ 267.1380, found 267.1382.

2,6-Diphenylhexane-1,4-diol (62) [24]



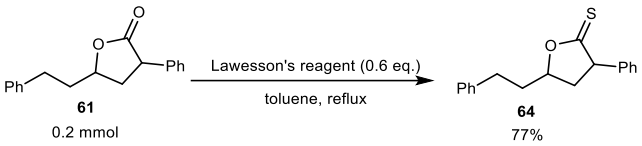
To a solution of **61** (0.2 mmol, 53.2 mg) in dry THF (2.0 mL), $LiAlH_4$ (0.8 mmol, 2 M in THF) was added at 0 °C under N_2 atmosphere. After stirring for 2 h at room temperature, the mixture was quenched with water and filtered through a pad of celite. The combined organic layer was dried over anhydrous Na_2SO_4 and removed under reduced pressure. The crude product was purified by column chromatography (PE: EA = 2:1) to afford to afford 49.1 mg (91 % yield, 57:43 dr) of **62** as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32 – 7.10 (m, 10H), 3.77 – 3.68 (m, 2.6H), 3.56 – 3.50 (m, 0.4H), 3.05 – 2.95 (m, 1H), 2.77 – 2.20 (m, 4H), 1.96 – 1.73 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.82, 142.75, 142.09, 142.05, 128.92, 128.85, 128.51, 128.49, 128.43, 127.94, 127.91, 126.95, 126.89, 125.93, 70.06, 69.54, 68.07, 67.31, 46.27, 44.87, 41.16, 40.77, 40.19, 38.82, 32.11, 32.08. HRMS m/z (ESI) calculated for $C_{18}H_{22}O_2$ $(M + H)^+$ 271.1693, found 271.1693.

4-Hydroxy-2,6-diphenyl-1-(pyrrolidin-1-yl)hexan-1-one (63) [25]



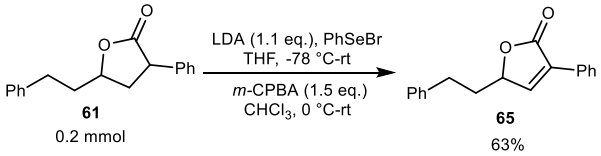
An oven-dried 25 mL Schlenk tube was charged with **61** (0.2 mmol, 53.2 mg), pyrrolidine (0.4 mmol, 33 μL) and Et_3N (0.8 mmol, 111 μL) and the resulting mixture was refluxed for 14 h. The reaction mixture was purified by flash column chromatography on silica gel (PE: EA = 2:1) to afford 56.1 mg (83 % yield, 55:45 dr) of **63** as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.30 – 7.13 (m, 10H), 4.01 (dd, *J* = 10.0, 3.2 Hz, 0.5H), 3.79 (dd, *J* = 8.2, 6.2 Hz, 0.5H), 3.66 – 3.06 (m, 6H), 2.80 – 2.58 (m, 2H), 2.42 – 2.26 (m, 1H), 1.91 – 1.69 (m, 7H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.51, 172.03, 142.45, 142.32, 139.97, 139.79, 128.88, 128.48, 128.44, 128.37, 128.35, 128.03, 126.99, 126.94, 125.72, 125.71, 69.99, 68.99, 49.11, 47.50, 46.47, 46.32, 46.18, 42.29, 42.06, 40.30, 39.96, 32.25, 30.51, 26.02, 25.99, 24.20, 24.09. HRMS m/z (ESI) calculated for $C_{22}H_{27}NO_2$ $(M + H)^+$ 338.2115, found 338.2113.

5-Phenethyl-3-phenyldihydrofuran-2(3H)-thione (64) [24]



To a solution of **61** (0.2 mmol, 53.2 mg) in dry toluene (2.0 mL), Lawesson's reagent (0.12 mmol, 48.5 mg) was added at room temperature and the resulting mixture was refluxed for 6 h. Then the reaction was cooled to room temperature and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (PE: EA = 4:1) to afford 43.6 mg (77% yield, 68:32 dr) of **64** as a yellow solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.31 – 7.15 (m, 10H), 4.96 – 4.91 (m, 0.3H), 4.76 – 4.70 (m, 0.7H), 4.27 – 4.24 (m, 0.3H), 4.01 – 3.97 (m, 0.7H), 2.90 – 2.67 (m, 2.8H), 2.43 – 2.33 (m, 0.6H), 2.26 – 2.12 (m, 1H), 2.06 – 1.92 (m, 1.6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.57, 139.74, 139.19, 129.07, 128.91, 128.79, 128.76, 128.58, 128.56, 127.88, 127.72, 126.47, 126.46, 87.81, 86.66, 61.24, 60.38, 40.26, 38.38, 36.82, 36.62, 32.32, 31.84. HRMS m/z (ESI) calculated for $C_{18}H_{18}OS$ $(M + H)^+$ 283.1151, found 283.1148.

5-Phenethyl-3-phenyldihydrofuran-2(3*H*)-one (65) [26]

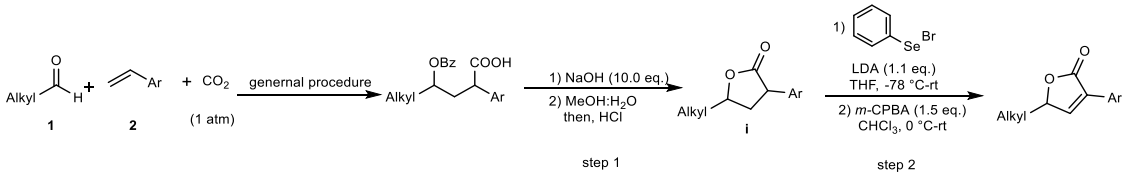


To a cold (−78 ℃) solution of LDA (0.22 mmol, 110 μL, 2 M THF complex in hexane) in dry THF (1.0 mL), a solution of 5-phenethyl-3-phenyldihydrofuran-2(3*H*)-one (53.2 mg, 0.2 mmol, dissolved in 0.5 mL THF) was added and the resulting mixture was stirred for 0.5 h at −78 °C. To the reaction mixture was added phenylselenenyl bromide (0.3 mmol, 1.5 eq., dissolve in 0.5 mL THF) and the resulting mixture was warmed to room temperature in period of 2 h. After completion, the solvent was removed under reduced pressure and the crude product was purified immediately by flash column chromatography on silica gel (PE: EA = 10: 1) to afford phenylselenenyl lactones. To a solution of phenylselenenyl lactones in $CHCl_3$ (1.0 mL), *m*-CPBA (0.3 mmol) was added at 0 ℃ and the resulting mixture was stirred at room temperature for 2 h. The mixture was added a further portion of $CHCl_3$ along with 5% aqueous Na_2CO_3, the

aqueous layer was extracted with DCM. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (PE: EA = 5:1) to afford 33.3 mg (63% yield) of **65** as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 (dd, *J* = 7.7, 2.0 Hz, 2H), 7.48 (t, *J* = 1.7 Hz, 1H), 7.44 – 7.39 (m, 3H), 7.34 – 7.30 (m, 2H), 7.26 – 7.22 (m, 3H), 5.03 (ddd, *J* = 8.3, 4.6, 1.8 Hz, 1H), 2.95 – 2.80 (m, 2H), 2.20 – 1.98 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.85, 148.02, 140.60, 131.79, 129.68, 129.51, 128.82, 128.74, 127.21, 126.55, 79.72, 34.99, 31.56. HRMS m/z (ESI) calculated for $C_{18}H_{18}O_2$ $(M + H)^+$ 265.1223, found 265.1225.

6.3 Synthesis of 3-aryl-5-alkyl-furan-2(5*H*)-one derivatives and their cytotoxicity assays

6.3.1 Synthesis of 3-aryl-5-alkyl-furan-2(5*H*)-one derivatives

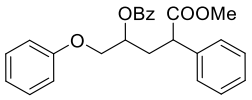


Step 1: To a solution of protected γ-hydroxy acid (1.0 eq.) in MeOH (0.1 M), H_2O (0.1 M) and NaOH (10.0 eq.) were added at room temperature. After stirring for 3 h at 70 °C, the mixture was acidified with 2 M HCl (to pH = 1). The reaction mixture was stirred at room temperature for another 3 h. After completion, the MeOH was removed under reduced pressure, the aqueous layer was extracted with EA. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the lactone derivative **(i)**.

Step 2: To a cold (−78 ℃) solution of LDA (1.1 eq.) in dry THF (0.2 M), a solution of **i** (1.0 eq., 0.4 M in THF) was added and the resulting mixture was stirred for 0.5 h at − 78 °C. To the reaction mixture was added a solution of phenylselenenyl bromide (1.5 eq., 0.6 M in THF) and the resulting mixture was warmed to room temperature in period of 2 h. After completion, the solvent was removed under reduced pressure and the crude product was purified immediately by flash column chromatography on silica gel (PE: EA = 10: 1) to afford phenylselenenyl lactones. To a solution of phenylselenenyl lactone in $CHCl_3$ (0.2 M), *m*-CPBA (1.5 eq.) was added at 0 ℃ and the resulting mixture was stirred at room temperature for 2 h. The mixture was added a further portion of $CHCl_3$

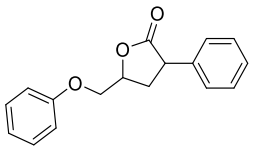
along with 5% aqueous Na_2CO_3, the aqueous layer was extracted with DCM. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the target compound.

5-Methoxy-5-oxo-1-phenoxy-4-phenylpentan-2-yl benzoate (66-1)



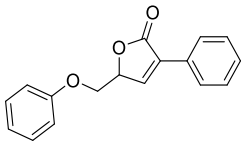
According to general procedure, the reaction was carried out with **1ae** (136.0 mg, 1.0 mmol), **2a** (345 μL, 3.0 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 15: 1, 58:42 dr) to afford 117.2 mg (29% yield, 58:42 dr) of **66-1** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (dd, *J* = 26.5, 7.7 Hz, 2H), 7.45 (q, *J* = 7.5 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.23 – 7.10 (m, 7H), 6.85 – 6.75 (m, 3H), 5.42 – 5.37 (m, 0.6H), 5.22 – 5.16 (m, 0.4H), 4.03 (dd, *J* = 26.0, 4.8 Hz, 2H), 3.75 – 3.69 (m, 1H), 3.50 (s, 1.7H), 3.41 (s, 1.3H), 2.75 – 2.60 (m, 1H), 2.32– 2.24 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.03, 173.72, 166.10, 165.95, 158.59, 158.50, 138.69, 138.20, 133.27, 133.17, 129.97, 129.90, 129.85, 129.80, 129.55, 129.52, 128.97, 128.92, 128.48, 128.40, 128.04, 127.85, 127.72, 127.59, 121.23, 121.21, 114.74, 114.70, 71.21, 70.92, 68.83, 68.77, 52.28, 52.16, 48.13, 47.84, 34.89, 34.84. HRMS m/z (ESI) calculated for $C_{25}H_{24}O_5$ $(M + H)^+$ 405.1697, found 405.1695.

5-(Phenoxymethyl)-3-phenyldihydrofuran-2(3*H*)-one (66-2)



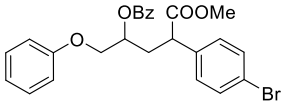
According to step 1, the reaction was carried out with **66-1** (117.2 mg, 0.29 mmol), H_2O (2.9 mL) and NaOH (148 mg, 2.9 mmol) in MeOH (2.9 mL). The crude product was purified by flash column chromatography on silica gel (with DCM) to afford 59.1 mg (76% yield, 54:46 dr) of **66-2** as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 – 7.27 (m, 7H), 7.00 – 6.90 (m, 3H), 4.94 – 4.89 (m, 0.5H), 4.85 – 4.79 (m, 0.5H), 4.23 – 4.09 (m, 2.5H), 3.91 (dd, *J* = 12.1, 9.2 Hz, 0.5H), 2.81 – 2.72 (m, 1H), 2.59 – 2.36 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.26, 176.38, 158.31, 158.25, 137.46, 136.65, 129.70, 129.66, 129.05, 128.95, 128.18, 127.88, 127.76, 127.68, 121.70, 121.57, 114.74, 76.01, 75.98, 69.45, 68.56, 46.57, 45.65, 33.43. HRMS m/z (ESI) calculated for $C_{17}H_{16}O_3$ $(M + H)^+$ 269.1172, found 269.1167.

5-(Phenoxymethyl)-3-phenylfuran-2(5*H*)-one (66)



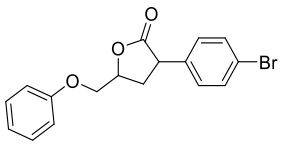
According to step 2, the reaction was carried out with **66-2** (53.6 mg, 0.2 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA= 10: 1) afford 18.6 mg (35% yield) of **66** as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 – 7.79 (m, 2H), 7.61 (d, *J* = 2.3 Hz, 1H), 7.35 – 7.32 (m, 3H), 7.22 (t, *J* = 7.6 Hz, 2H), 6.94 – 6.82 (m, 3H), 5.30 – 5.27 (m, 1H), 4.27 – 4.08 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.27, 158.12, 144.95, 133.03, 129.77, 129.73, 129.39, 128.84, 127.26, 121.88, 114.84, 78.37, 67.93. HRMS m/z (ESI) calculated for $C_{17}H_{14}O_3$ $(M + H)^+$ 267.1016, found 267.1016.

4-(4-Bromophenyl)-5-methoxy-5-oxo-1-phenoxypentan-2-yl benzoate (67-1)



According to general procedure, the reaction was carried out with **1ae** (136.0 mg, 1.0 mmol), **2d** (392 μL, 3.0 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 15: 1) to afford 178.4 mg (37% yield, 53:47 dr) of **67-1** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 – 7.84 (m, 2H), 7.51 – 7.44 (m, 1H), 7.38 – 7.29 (m, 4H), 7.19 – 7.06 (m, 4H), 6.88 – 6.76 (m, 3H), 5.41 – 5.35 (m, 0.5H), 5.21 – 5.16 (m, 0.5H), 4.04 (dd, *J* = 20.2, 4.8 Hz, 2H), 3.69 (dt, *J* = 8.3, 6.6 Hz, 1H), 3.53 (s, 1.6H), 3.43 (s, 1.4H), 2.72 – 2.57 (m, 1H), 2.31 – 2.24 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.60, 173.32, 166.06, 165.95, 158.53, 158.43, 137.65, 137.18, 133.39, 133.29, 132.10, 132.02, 129.87, 129.83, 129.79, 129.76, 129.64, 129.61, 129.58, 128.55, 128.44, 121.81, 121.63, 121.33, 114.75, 114.71, 71.11, 70.67, 68.81, 68.67, 52.45, 52.33, 47.57, 47.53, 34.79, 34.69. HRMS m/z (ESI) calculated for $C_{25}H_{23}BrO_5$ $(M + H)^+$ 483.0802, found 483.0803.

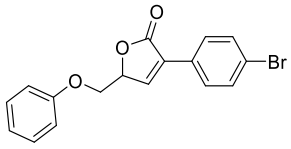
3-(4-Bromophenyl)-5-(phenoxymethyl)dihydrofuran-2(3*H*)-one (70)



According to step 1, the reaction was carried out with **67-1** 178.4 mg (0.37 mmol), H_2O (3.7 mL) and NaOH (148 mg, 3.7 mmol) in MeOH (3.7 mL). The crude product was purified by flash column chromatography on silica gel (with DCM) to afford 93.4 mg (73% yield, 53:47 dr) of **70** as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 – 7.47 (m, 2H), 7.32 – 7.28 (m, 2H), 7.23 – 7.18 (m, 2H), 7.02 – 6.97 (m, 1H), 6.93 – 6.89 (m, 2H), 4.95 – 4.90 (m, 0.5H), 4.87 – 4.81 (m, 0.5H), 4.26 – 4.10 (m, 2.5H), 3.91 (dd, *J* = 12.1, 9.3 Hz, 0.5H), 2.83 – 2.76 (m, 1H), 2.58 – 2.36 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.76, 175.85, 158.22, 158.16, 136.38, 135.57, 132.16, 132.08, 129.92, 129.76, 129.72, 129.69, 121.86, 121.83, 121.75, 121.70, 114.72, 76.05, 75.90,

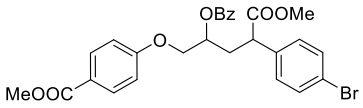
69.44, 68.37, 46.04, 45.08, 33.30, 33.14. HRMS m/z (ESI) calculated for $C_{17}H_{15}BrO_3$ $(M + H)^+$ 347.0277, found 347.0281.

3-(4-Bromophenyl)-5-(phenoxymethyl)furan-2(5*H*)-one (67)



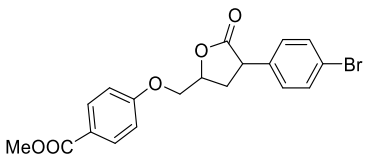
According to step 2, the reaction was carried out with **70** (69.2 mg, 0.2 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA= 10: 1) afford 17.9 mg (26 % yield) of **67** as a white solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.70 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 1.9 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 2H), 5.29 (td, *J* = 5.4, 1.9 Hz, 1H), 4.27 (dd, *J* = 9.9, 5.2 Hz, 1H), 4.11 (dd, *J* = 9.9, 5.7 Hz, 1H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.97, 158.05, 145.32, 132.08, 132.05, 129.81, 128.80, 128.24, 124.18, 121.98, 114.83, 78.43, 67.76. All data are in accordance with the literature.[23]

Methyl 4-((2-(benzoyloxy)-4-(4-bromophenyl)-5-methoxy-5-oxopentyl)oxy)benzoate (68-1)



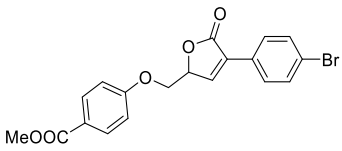
According to general procedure, the reaction was carried out with **1af** (194.1 mg, 1.0 mmol), **2d** (392 μL, 3.0 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 8: 1) to afford 140.4 mg (26 % yield, 58:42 dr) of **68-1** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.95 – 7.84 (m, 4H), 7.51 – 7.46 (m, 1H), 7.39 – 7.29(m, 4H), 7.11 – 7.07 (m, 2H), 6.84 – 6.78 (m, 2H), 5.43– 5.38 (m, 0.6H), 5.21– 5.16 (m, 0.4H), 4.09 (dd, *J* = 27, 4.8 Hz, 2H), 3.78 (d, *J* = 2.3 Hz, 3H), 3.70 – 3.66 (m, 1H), 3.53 (s, 1.7H), 3.44 (s, 1.3H), 2.72 – 2.57 (m, 1H), 2.30 – 2.24 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.51, 173.23, 166.78, 166.02, 165.90, 162.16, 162.06, 137.54, 137.01, 133.50, 133.40, 132.13, 132.05, 131.70, 131.68, 129.85, 129.79, 129.74, 129.58, 128.58, 128.48, 123.23, 121.87, 121.68, 114.29, 114.25, 70.81, 70.32, 68.95, 68.78, 52.48, 52.37, 51.97, 47.49, 34.69, 34.66. HRMS m/z (ESI) calculated for $C_{27}H_{25}BrO_7$ $(M + H)^+$ 541.0856, found 541.0862.

Methyl 4-((4-(4-bromophenyl)-5-oxotetrahydrofuran-2-yl)methoxy)benzoate (68-2)



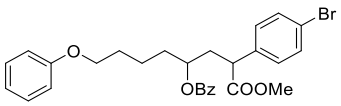
According to step 1, the reaction was carried out with **68-1** (140.4 mg, 0.26 mmol), H_2O (2.6 mL) and NaOH (104.0 mg, 2.6 mmol) in MeOH (2.6 mL). The crude product was purified by flash column chromatography on silica gel (with DCM) to afford 85.1 mg (81% yield, 58:42 dr) of **68-2** as a white solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.93 (dd, *J* = 8.8, 3.7 Hz, 2H), 7.43 (dd, *J* = 8.5, 2.8 Hz, 2H), 7.13 (t, *J* = 8.4 Hz, 2H), 6.86 (t, *J* = 8.4 Hz, 2H), 4.91 – 4.88 (m, 0.4H), 4.84 – 4.79 (m, 0.6H), 4.25 – 4.23 (m, 1H), 4.15 – 4.10 (m, 1H), 3.87 (t, *J* = 9.5 Hz, 0.4H), 3.87 (dd, *J* = 12.1, 9.2 Hz, 0.6H), 3.82 (d, *J* = 1.7 Hz, 3H), 2.79 – 2.70 (m, 1H), 2.54 – 2.31 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.54, 175.64, 166.75, 161.82, 161.74, 136.17, 135.34, 132.24, 132.16, 131.85, 131.82, 129.88, 129.63, 123.79, 123.65, 121.99, 121.88, 114.30, 114.28, 75.72, 75.59, 69.50, 68.44, 52.10, 52.08, 46.00, 45.03, 33.17, 33.12. HRMS m/z (ESI) calculated for $C_{19}H_{17}BrO_5$ $(M + H)^+$ 405.0332, found 405.0330.

Methyl 4-((4-(4-bromophenyl)-5-oxo-2,5-dihydrofuran-2-yl)methoxy)benzoate (68)



According to step 2, the reaction was carried out with **68-2** (80.8 mg, 0.2 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA= 5: 1) afford 25.7 mg (32 % yield) of **68** as a white solid: **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.02 – 7.99 (m, 2H), 7.79 – 7.70 (m, 2H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.58 – 7.55 (m, 2H), 6.93 – 6.90 (m, 2H), 5.39 (td, *J* = 5.2, 1.9 Hz, 1H), 4.37 (dd, *J* = 9.9, 5.2 Hz, 1H), 4.27 (dd, *J* = 9.9, 5.3 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.78, 166.74, 161.61, 144.63, 132.38, 132.13, 131.87, 128.80, 128.08, 124.33, 123.89, 114.34, 78.13, 67.67, 52.13. All data are in accordance with the literature.[23]

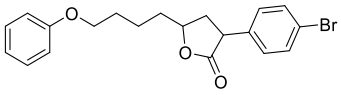
2-(4-Bromophenyl)-1-methoxy-1-oxo-8-phenoxyoctan-4-yl benzoate (69-1)



According to general procedure, the reaction was carried out with **1ag** (178.1 mg, 1.0 mmol), **2d** (392 μL, 3.0 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 15: 1) to afford 246.3 mg (47 % yield, 60:40 dr) of **69-1** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 (dd, *J* = 29.5, 7.4 Hz, 2H), 7.47 (q, *J* = 6.9 Hz, 1H), 7.48 – 7.27 (m, 4H), 7.18 – 7.04 (m, 4H), 6.84 – 6.74 (m,

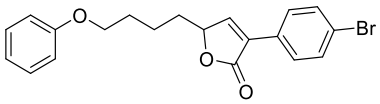
3H), 5.16 – 5.10 (m, 0.6H), 4.98 – 4.91 (m, 0.4H), 3.85 – 3.79 (m, 2H), 3.59 (dt, *J* = 12.4, 6.4 Hz, 1H), 3.52 (s, 1.8H), 3.39 (s, 1.2H), 2.51 – 2.39 (m, 1H), 2.09 – 1.97 (m, 1H), 1.75 – 1.40 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.77, 173.43, 166.21, 166.07, 159.04, 159.02, 137.87, 137.48, 133.16, 133.06, 132.03, 131.94, 130.22, 130.20, 129.83, 129.73, 129.61, 129.57, 129.48, 128.51, 128.42, 121.67, 121.48, 120.64, 114.55, 72.92, 72.57, 67.44, 67.41, 52.35, 52.21, 47.80, 47.69, 37.93, 37.81, 34.49, 34.37, 29.13, 29.11, 21.85, 21.79. HRMS m/z (ESI) calculated for $C_{28}H_{29}BrO_5$ $(M + H)^+$ 525.1271, found 525.1274.

3-(4-Bromophenyl)-5-(4-phenoxybutyl)dihydrofuran-2(3*H*)-one (69-2)



According to step 1, the reaction was carried out with **69-1** (246.3 mg, 0.47 mmol), H_2O (4.7 mL) and NaOH (188.0 mg, 4.7 mmol) in MeOH (4.7 mL). The crude product was purified by flash column chromatography on silica gel (with DCM) to afford 147.7 mg (81% yield, 50:50 dr) of **69-2** as a white solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.23 – 7.19 (m, 2H), 7.10 (dd, *J* = 8.3, 4.9 Hz, 2H), 6.87 (t, *J* = 7.3 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 2H), 4.60 – 4.55 (m, 0.5H), 4.48 – 4.42 (m, 0.5H), 3.92 (t, *J* = 6.2 Hz, 2H), 3.81 – 3.76 (m, 1H), 2.72 – 2.67 (m, 0.5H), 2.44 – 2.31 (m, 1H), 1.98 – 1.91 (m, 0.5H), 1.87 – 1.55 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.67, 176.27, 159.01, 136.11, 135.54, 132.20, 132.06, 129.91, 129.59, 129.46, 121.78, 121.74, 120.80, 114.56, 78.85, 78.63, 67.41, 46.73, 45.06, 37.89, 36.15, 35.24, 35.17, 29.09, 29.05, 22.33, 22.22. HRMS m/z (ESI) calculated for $C_{20}H_{21}BrO_3$ $(M + H)^+$ 389.0747, found 389.0749.

3-(4-Bromophenyl)-5-(4-phenoxybutyl)furan-2(5*H*)-one (69)



According to step 2, the reaction was carried out with **69-2** (77.6 mg, 0.2 mmol). The crude product was purified by flash column chromatography on silica gel (PE: EA = 5: 1) afford 29.7 mg (39 % yield) of **69** as a white solid: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.47 (t, *J* = 8.4 Hz, 3H), 7.20 (t, *J* = 7.8 Hz, 2H), 6.88 – 6.80 (m, 3H), 4.98 (t, *J* = 6.5 Hz, 1H), 3.90 (t, *J* = 6.3 Hz, 2H), 1.89 – 1.68 (m, 4H), 1.65 – 1.58 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.44, 158.96, 148.16, 131.98, 130.84, 129.59, 128.71, 128.49, 123.82, 120.84, 114.57, 80.56, 67.35, 33.34, 29.09, 22.07. HRMS m/z (ESI) calculated for $C_{20}H_{19}BrO_3$ $(M + H)^+$ 387.0590, found 387.0590.

6.3.2 Cell culture and cytotoxicity assay

All cell lines were cultured in an incubator at 37 °C with 5% CO_2. 4T1, CT26 and LLC cells were cultured in Roswell Park Memorial Institute medium 1640 (RPMI-1640) containing 10% fetal bovine serum (FBS) and 1% dual antibody. Hela cells were cultured in Dulbecco's Modified Eagle Medium (DMEM) containing 10% FBS and 1% streptomycin.

The cells were homogeneously inoculated in a 96-well plate and 200 μL of culture medium was added to each well. Subsequently, the drug was diluted to different concentrations with serum-free medium, and 200 μL of the prepared drug was added to each well to treat the cells. After 24 h of incubation, 20 μL MTT (5 mg/mL) solution was added to each well and incubated for 4 h. The culture solution was carefully aspirated and 200 μL of DMSO was added to each well to dissolve the generated formazan crystals. The absorbance value of each well was read at 492 nm using an enzyme marker.

Cell survival was calculated according to the following formula:

Cell viability = Absorbance of experimental groups/Absorbance of control group × 100%

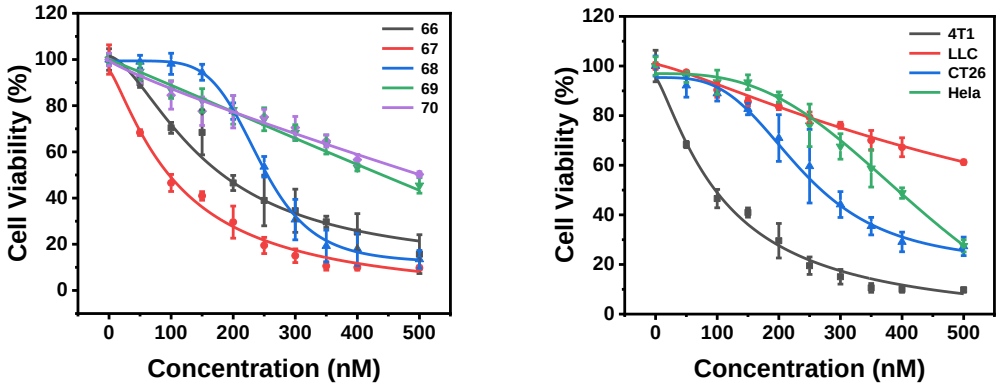
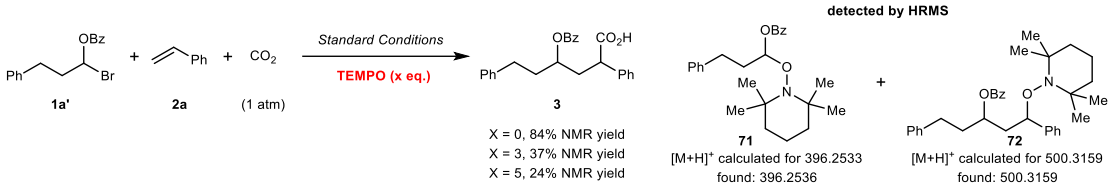


Figure S3. Cytotoxicity assay. The cell viability of compounds **66-70** against 4T1 cell lines (left), the cell viability of compound **67** against 4T1, Hela, LLC and CT26 cell lines (right). Data are presented as mean values ± SD (n = 3 biologically independent samples).

7. Mechanistic Studies

7.1 Radical-trapping experiments



In glovebox, an oven-dried 25 mL Schlenk tube was charged with **1a'** (0.2mmol, 63.6mg, 1.0 eq), 3DPAFIPN (6.5 mg, 0.01 mmol, 5 mol%), K_3PO_4 (42.0 mg, 0.2 mmol, 1.0 eq.), 5 Å MS (100.0 mg) and TEMPO (x eq.). The tube was removed from glovebox and then evacuated and back-filled with CO_2 for 3 times. To the tube was added DMA (2.0 mL), **2a** (69 μL, 0.60 mmol, 3.0 eq.) and TMEDA (90 μL, 0.60 mmol, 3.0 eq.) under CO_2 atmosphere at room temperature. The tube was then charged with CO_2 at −78 °C for another 2 minutes and stirred at −10 °C under blue LEDs (455 nm, 15W) irradiation for 12 h. The reaction mixture was diluted with 2.0 mL of EA and quenched by 2.0 mL of 2 M HCl (aq.). After stirring for 15 min at room temperature, the mixture was extracted with EA, the combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The yield of target product **3** was detected by ^1H NMR analysis with CH_2Br_2 (7.0 μL, 0.1 mmol) as an internal standard. The TEMPO-trapped products **71** and **72** were detected by HRMS.

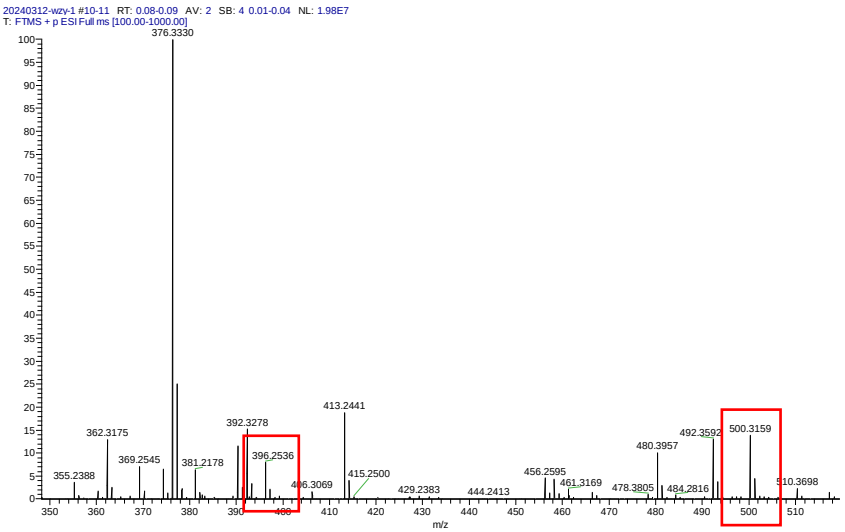
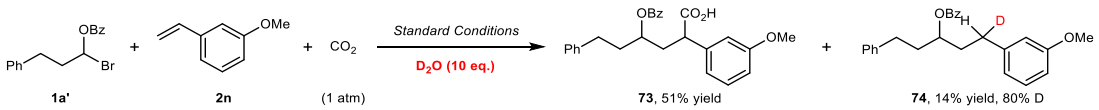
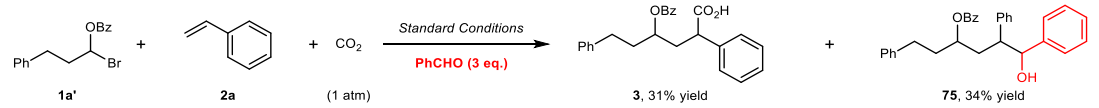


Figure S4. The HRMS of radical-trapping experiments

7.2 Carbon anion trapping experiments.



In glovebox, an oven-dried 25 mL Schlenk tube was charged with **1a'**, 3DPAFIPN (6.5 mg, 0.01 mmol, 5 mol%), K_3PO_4 (42.0 mg, 0.2 mmol, 1.0 eq.) and 5 Å MS (100.0 mg). The tube was removed from glovebox and then evacuated and back-filled with CO_2 for 3 times. To the mixture was added DMA (2.0 mL), **2n** (83 μL, 0.60 mmol, 3.0 eq.), TMEDA (90 μL, 0.60 mmol, 3.0 eq.) and D_2O (36 μL, 2.0 mmol, 10.0 eq.) under CO_2 atmosphere at room temperature. The tube was then charged with CO_2 at −78 °C for another 2 minutes and stirred at –10 °C under blue LEDs (455 nm, 15W) irradiation for 12 h. The reaction mixture was diluted with 2.0 mL of EA and quenched by 2.0 mL of 2 M HCl (aq.). After stirring for 15 min at room temperature, the aqueous layer was extracted with EA, the combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The yield of target product **73** (51%) was detected by ^{1}H NMR analysis with CH_2Br_2 (7.0 μL, 0.1 mmol) as an internal standard. The crude product was purified by flash column chromatography on silica gel (PE: EA = 50: 1) to afford 10.4 mg (14% yield, 80% D) of **74** as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 – 7.97 (m, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.21 – 7.08 (m, 7H), 6.69 – 6.63 (m, 3H), 5.21 – 5.15 (m, 1H), 3.69 (s, 3H), 2.68 – 2.56 (m, 3H), 2.06 – 1.89 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.43, 159.81, 143.25, 141.65, 133.02, 130.67, 129.73, 129.54, 128.57, 128.50, 128.46, 126.08, 120.84, 114.21, 111.45, 74.20, 55.26, 36.22, 36.06, 35.99, 31.87. HRMS m/z (ESI) calculated for $C_{25}H_{25}DO_3$ $(M + Na)^+$ 398.1837, found 398.1833.



In glovebox, an oven-dried 25 mL Schlenk tube was charged with **1a'**, 3DPAFIPN (6.5 mg, 0.01 mmol, 5 mol%), K_3PO_4 (42.0 mg, 0.2 mmol, 1.0 eq.) and 5 Å MS (100.0 mg). The tube was removed from glovebox and then evacuated and back-filled with CO_2 for 3 times. To the mixture was added DMA (2.0 mL), **2a** (69 μL, 0.60 mmol, 3.0 eq.), TMEDA (90 μL, 0.60 mmol, 3.0 eq.) and benzaldehyde (61 μL, 0.6 mmol, 3.0 eq.) under CO_2 atmosphere at room temperature. The tube was then charged with CO_2 at − 78 °C for another 2 minutes and stirred at –10 °C under blue LEDs (455 nm, 15W)

irradiation for 12 h. The reaction mixture was diluted with 2.0 mL of EA and quenched by 2.0 mL of 2 M HCl (aq.). After stirring for 15 min at room temperature, the aqueous layer was extracted with EA, the combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The yield of target product **3** (31%) was detected by ^1H NMR analysis with CH_2Br_2 (7.0 μL, 0.1 mmol) as an internal standard. The crude product was purified by flash column chromatography on silica gel (PE: EA = 7: 1) to afford 30.2 mg (34% yield) of addition product **75** as a yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.85 (dd, *J* = 18.6, 7.4 Hz, 2H), 7.57 – 7.48 (m, 1H), 7.41 – 7.01 (m, 17H), 5.09 – 4.71 (m, 2H), 3.11 – 2.93 (m, 1H), 2.64 – 2.25 (m, 3H), 2.20 – 2.14 (m, 1H), 1.99 – 1.79 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.31, 166.13, 142.96, 142.71, 142.29, 141.72, 141.62, 141.56, 141.26, 140.91, 140.07, 132.86, 132.78, 130.55, 130.46, 129.70, 129.63, 128.90, 128.79, 128.67, 128.50, 128.47, 128.43, 128.38, 128.36, 128.28, 128.23, 128.16, 128.03, 127.47, 127.42, 127.31, 127.02, 126.84, 126.73, 126.40, 125.98, 125.93, 78.79, 78.56, 74.09, 73.35, 73.13, 51.02, 50.77, 50.10, 36.56, 35.66, 35.43, 35.22, 34.66, 33.92, 31.66, 31.37, 31.30. HRMS m/z (ESI) calculated for $C_{31}H_{30}O_3$ $(M + Na)^+$ 473.2087, found 473.2083.

7.3 Fluorescence quenching experiments

Fluorescence quenching experiments were measured on a Fluorescence Spectrophotometer F-7100.

General Procedure for fluorescence quenching experiments:

In glovebox, increasing amount of TMEDA, and **1a'** to a 2.5 mL solution of 3DPAFIPN in DMA (5.0×10^{-5} M) in 4.0 mL quartz cuvette (d = 1 cm) and covered with Teflon cap. Then the emission spectrums of the solution were collected after each addition.

TMEDA: A stock solution of TMEDA (0.5 M) was prepared. Then, different amounts of this stock solution were added to 2.5 mL of 3DPAFIPN in DMA ($5*10^{-5}$ M).

1a': A stock solution of **1a'** (0.5 M) was prepared. Then, different amounts of this stock solution were added to 2.5 mL of 3DPAFIPN in DMA ($5*10^{-5}$ M).

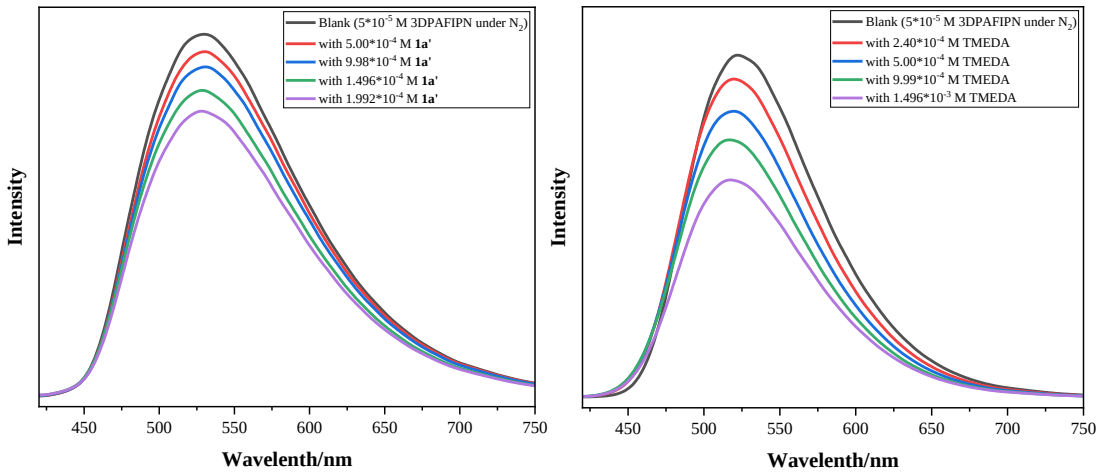


Figure S5. Optical experiment with fluorescence spectrum. Stern–Volmer experiment of 3DPAFIPN with **1a'** (left), Stern–Volmer experiment of 3DPAFIPN with TMEDA (right).

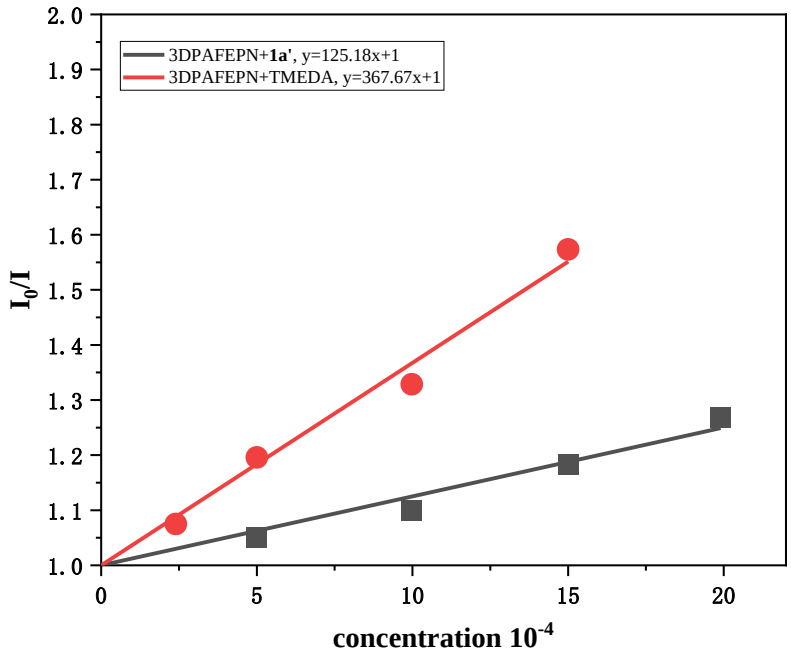
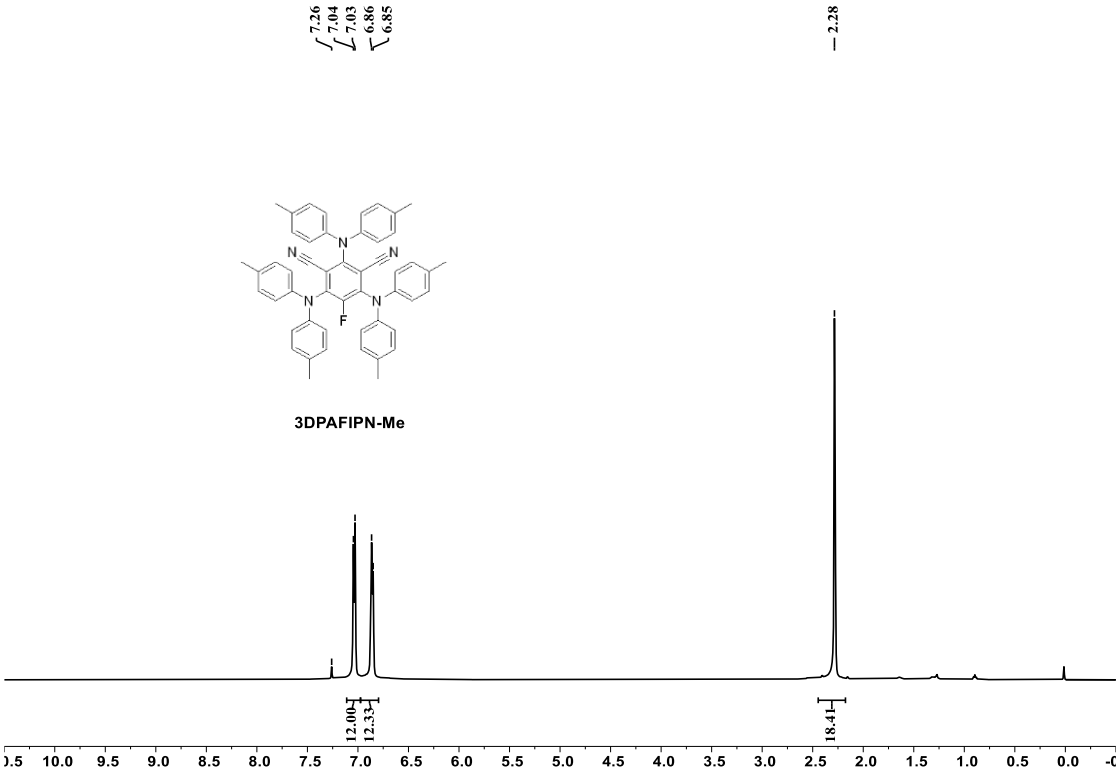


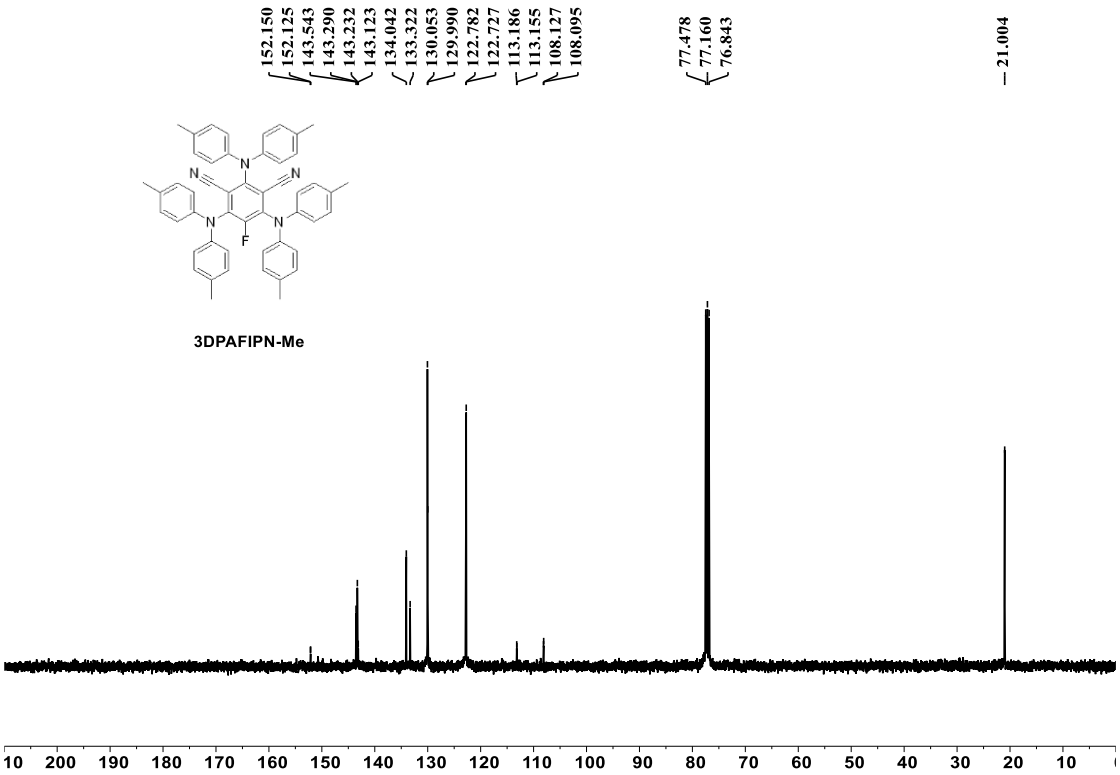
Figure S6. Stern-Volmer luminescence studies

8. Copies of NMR Spectra

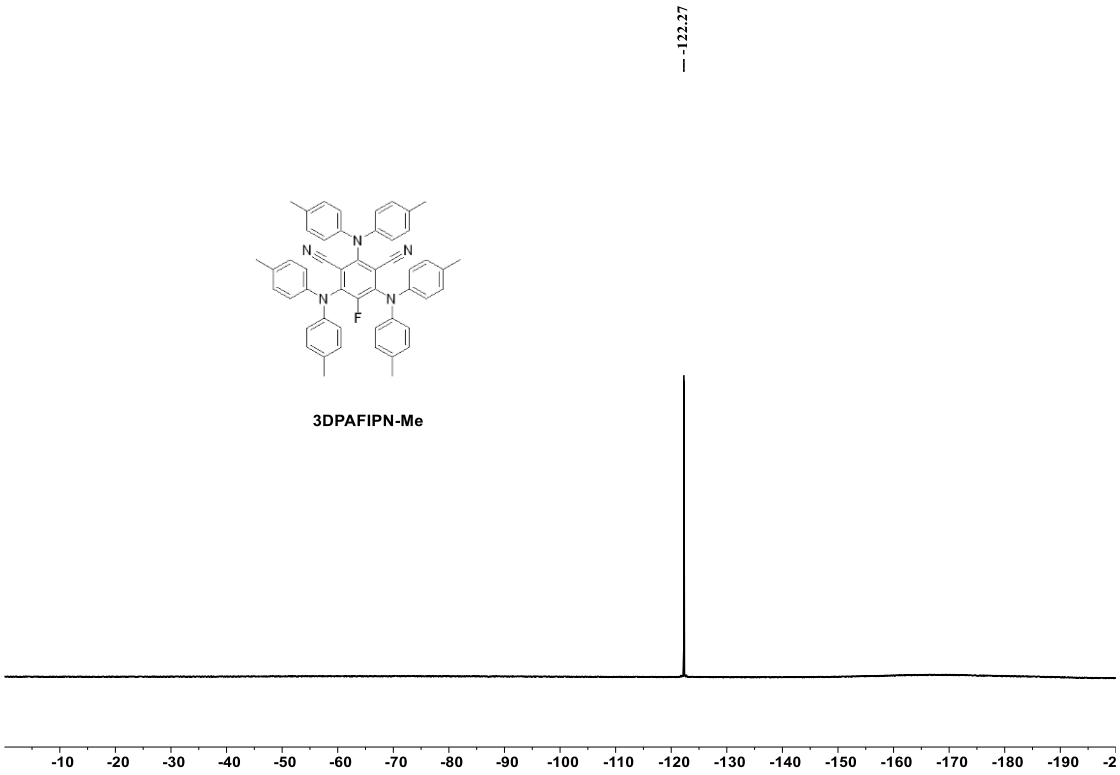
^{1}H NMR (500 MHz, $CDCl_3$)



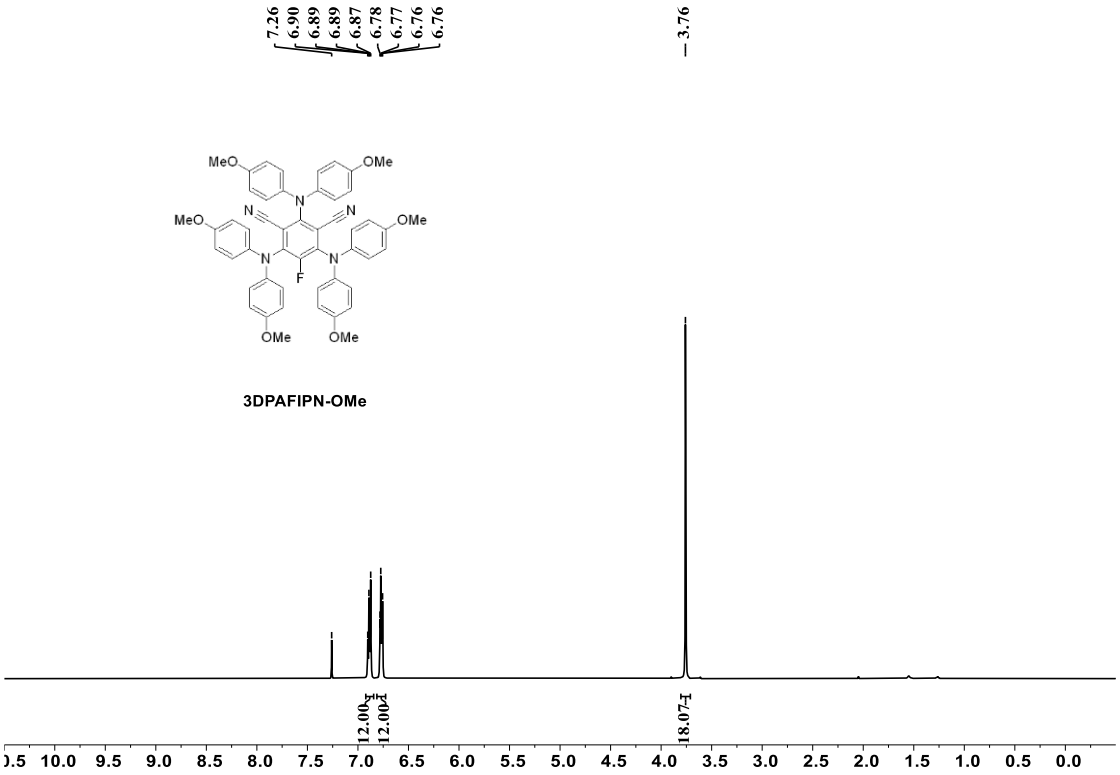
^{13}C NMR (101 MHz, $CDCl_3$)



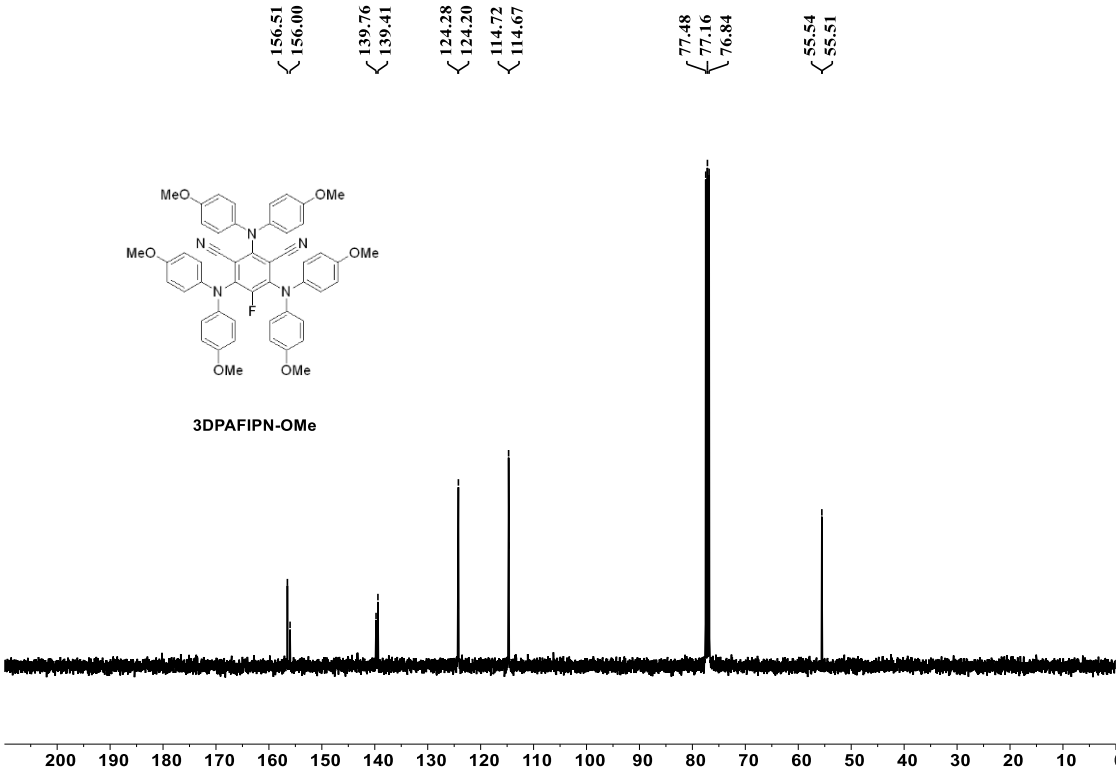
^{19}F NMR (377 MHz, $CDCl_3$)



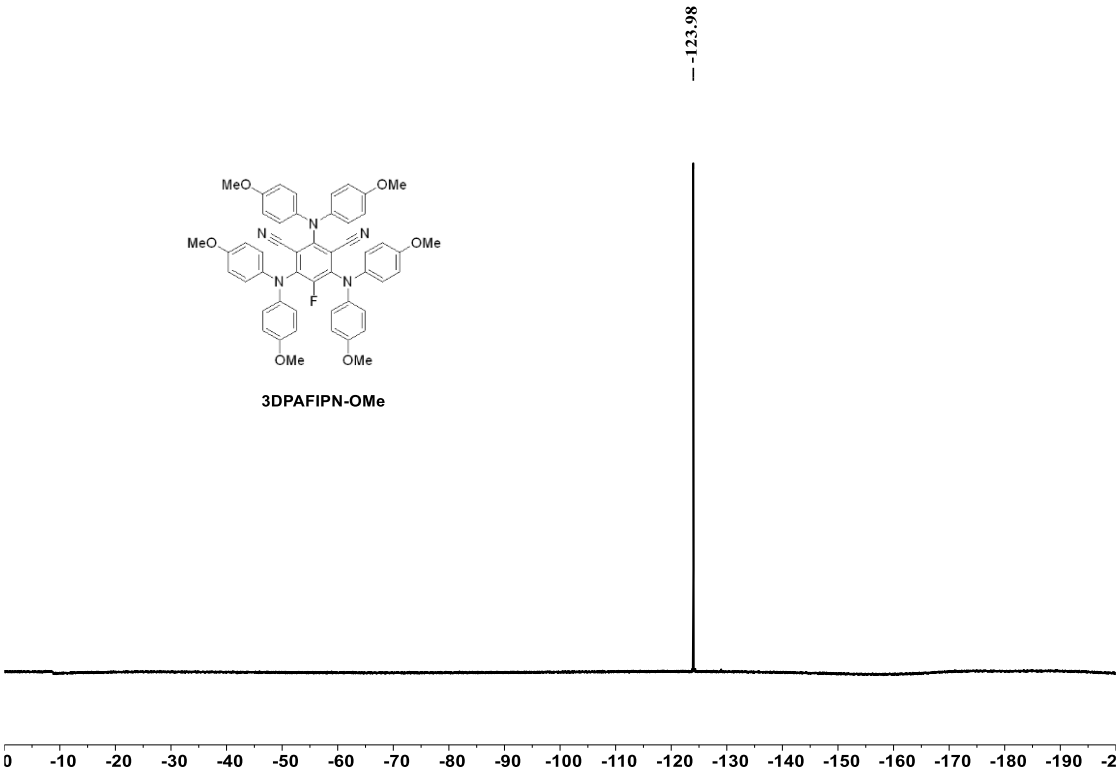
^{1}H NMR (500 MHz, $CDCl_3$)



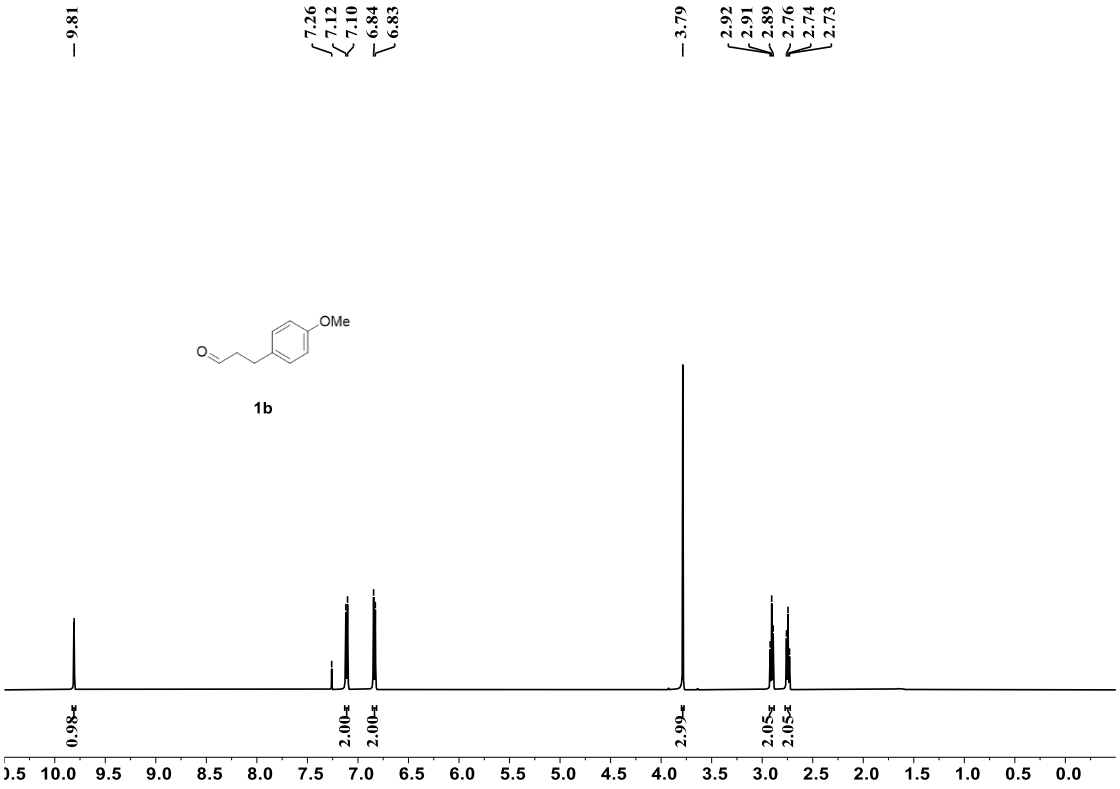
^{13}C NMR (101 MHz, $CDCl_3$)



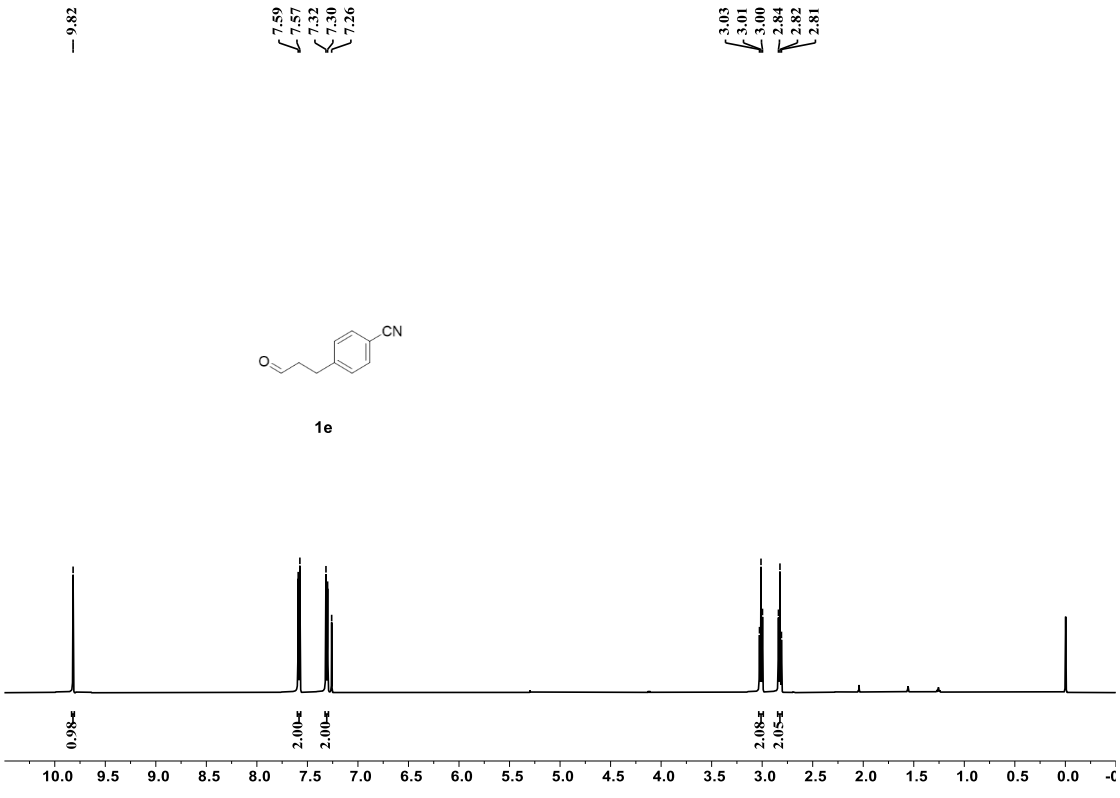
^{19}F NMR (377 MHz, $CDCl_3$)



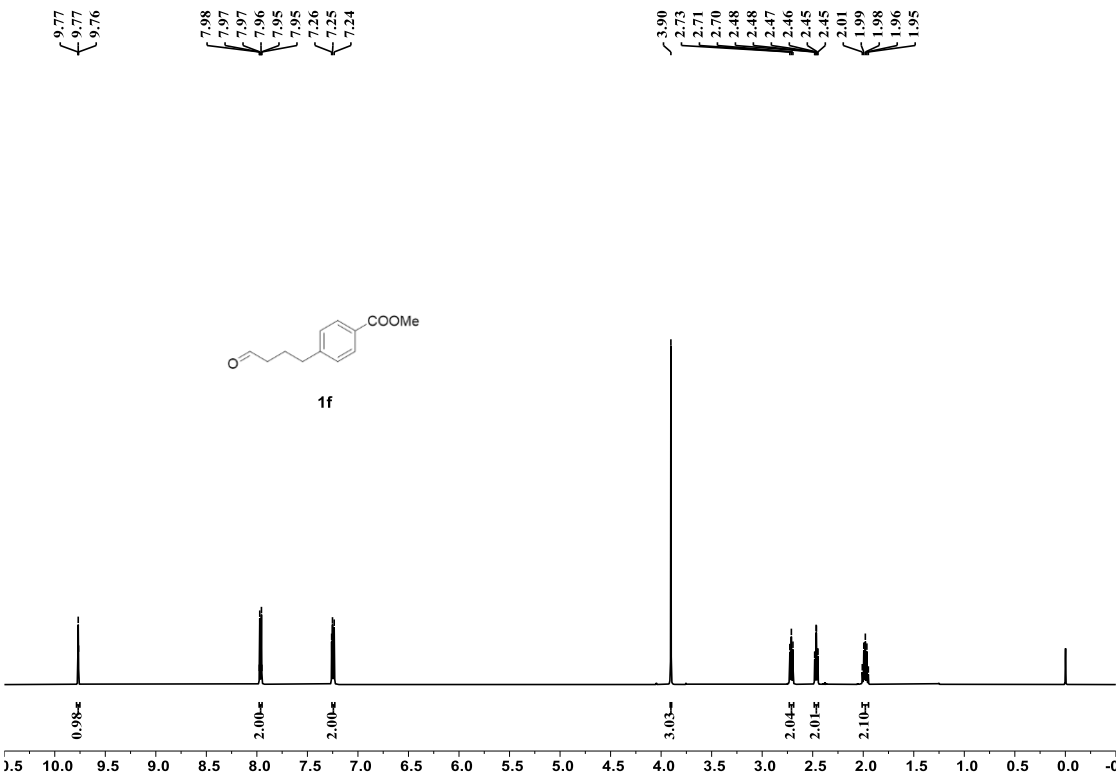
^{1}H NMR (500 MHz, $CDCl_3$)



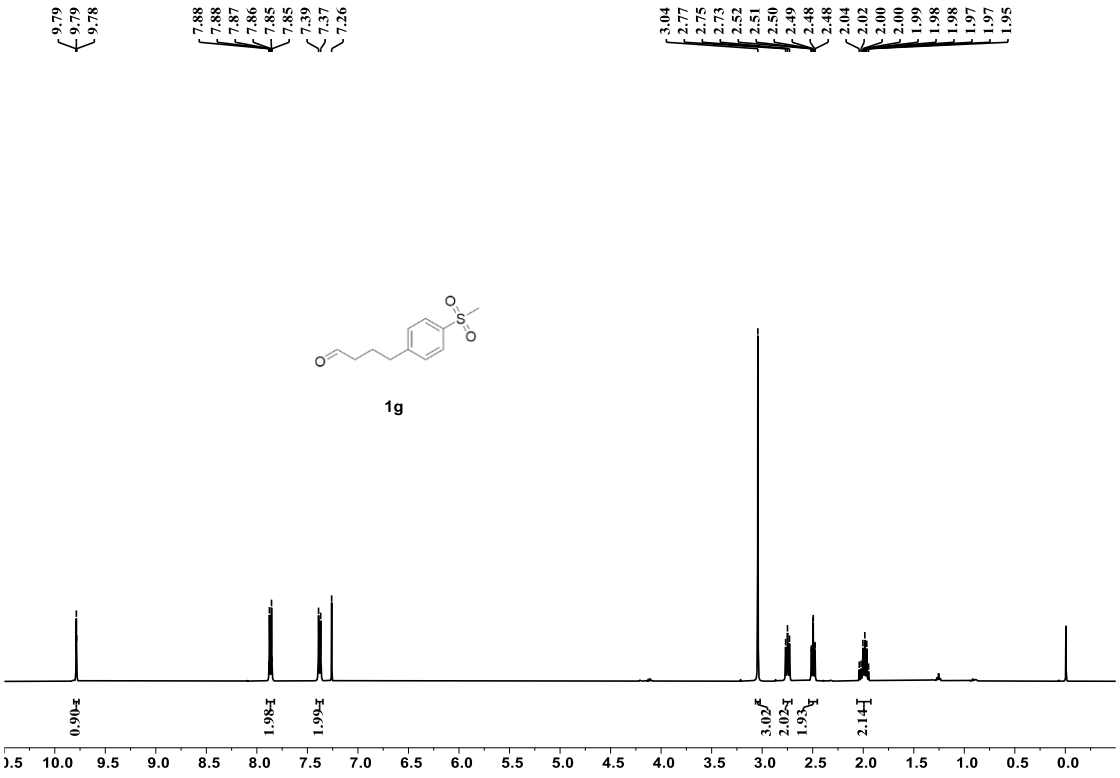
^{1}H NMR (500 MHz, $CDCl_3$)



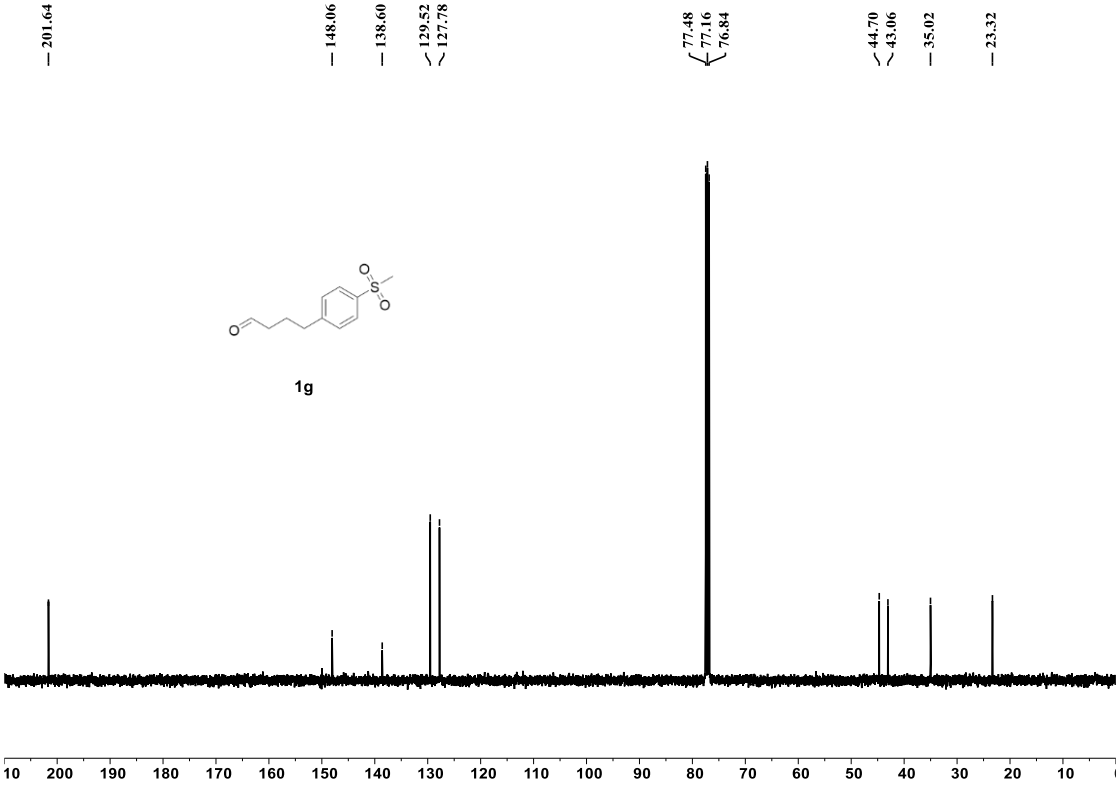
^{1}H NMR (500 MHz, $CDCl_3$)



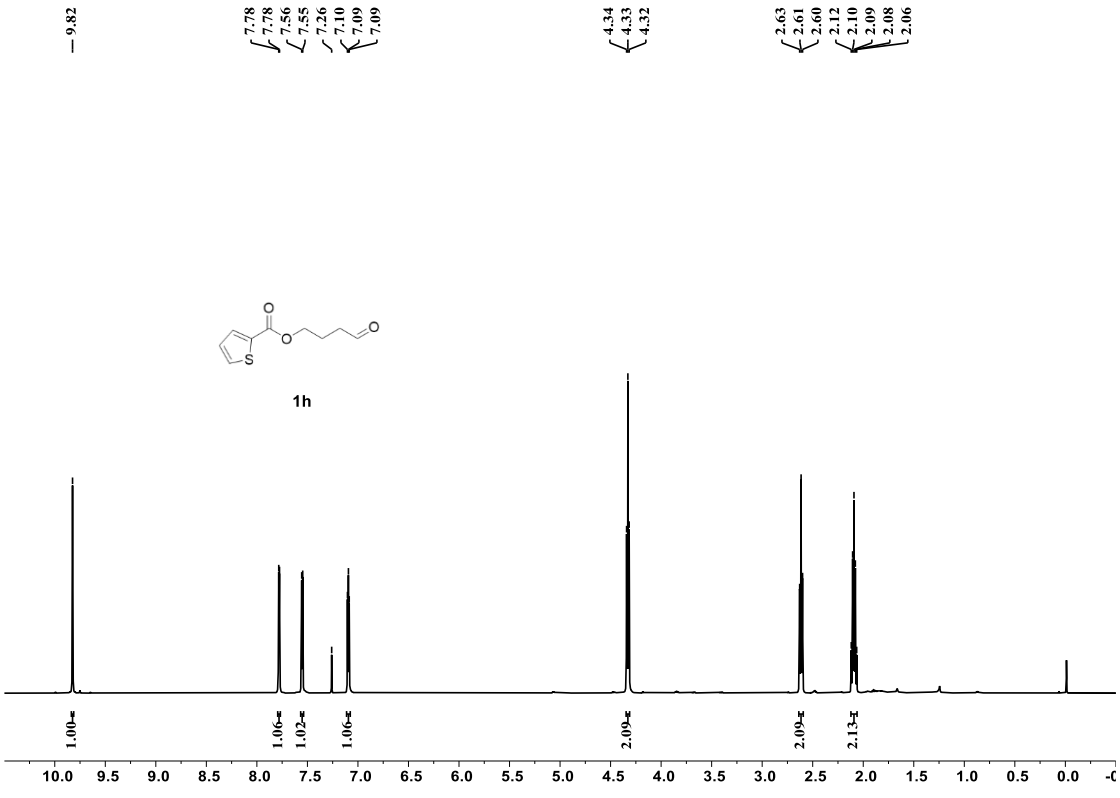
^{1}H NMR (400 MHz, $CDCl_3$)



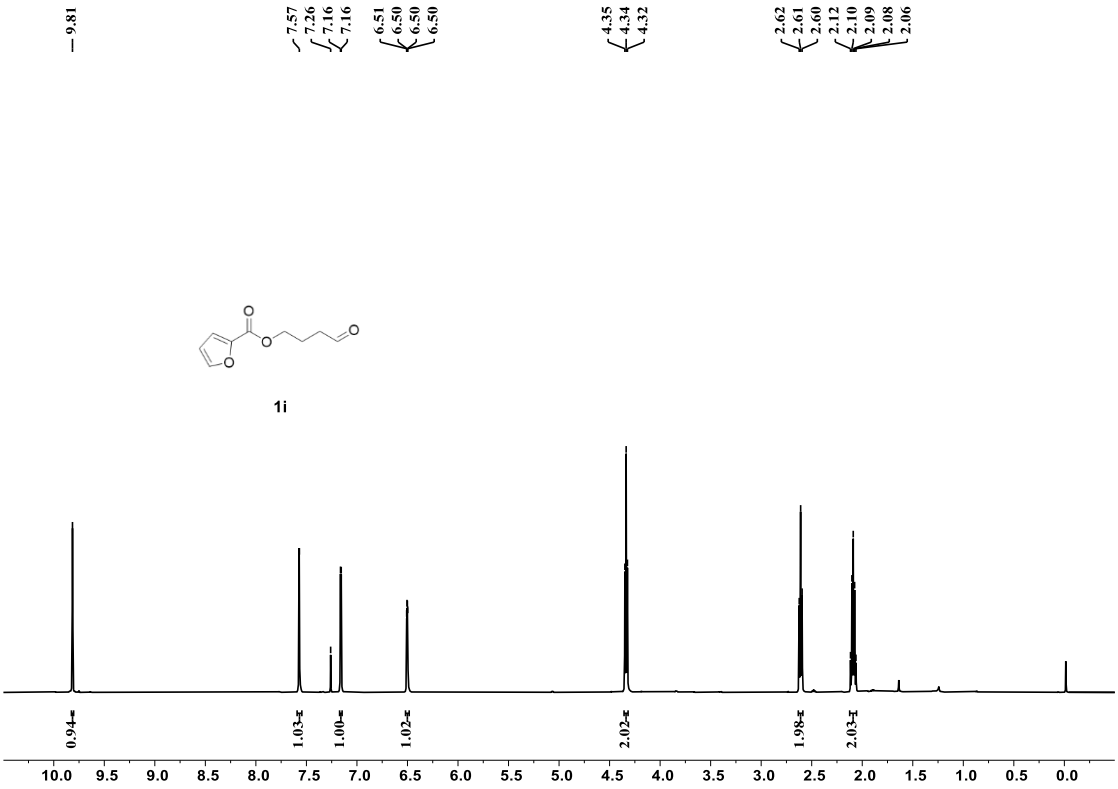
^{13}C NMR (101 MHz, $CDCl_3$)



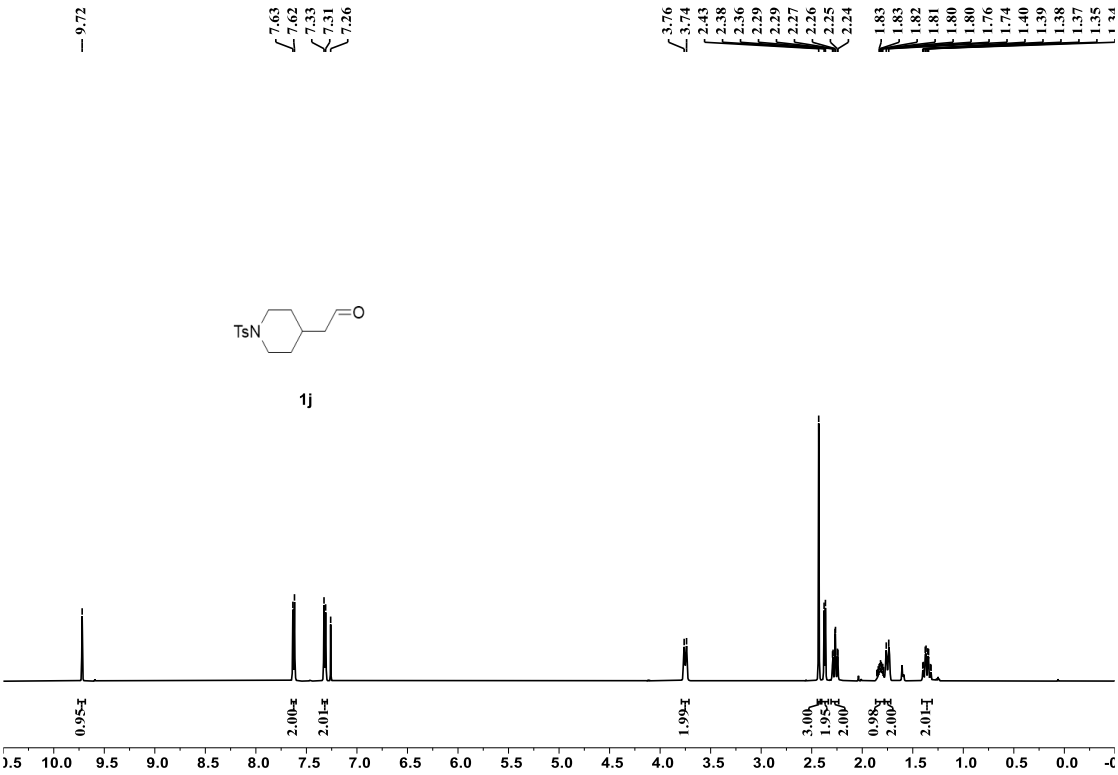
^{1}H NMR (500 MHz, $CDCl_3$)



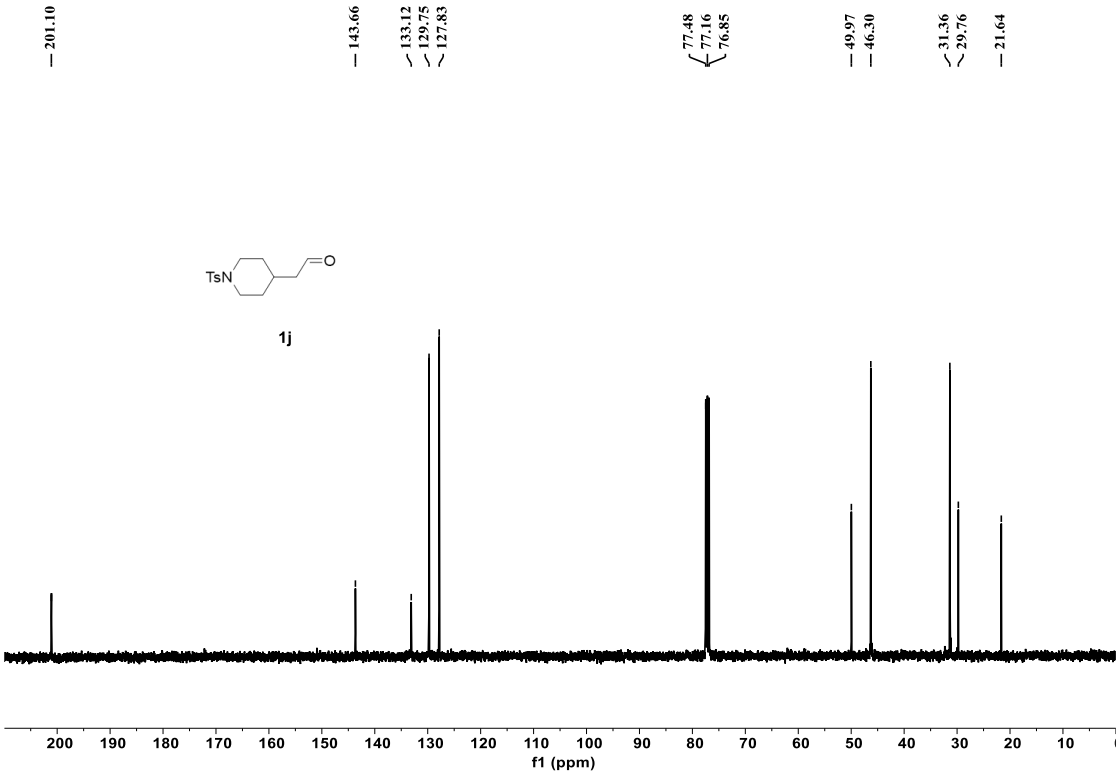
^{1}H NMR (500 MHz, $CDCl_3$)



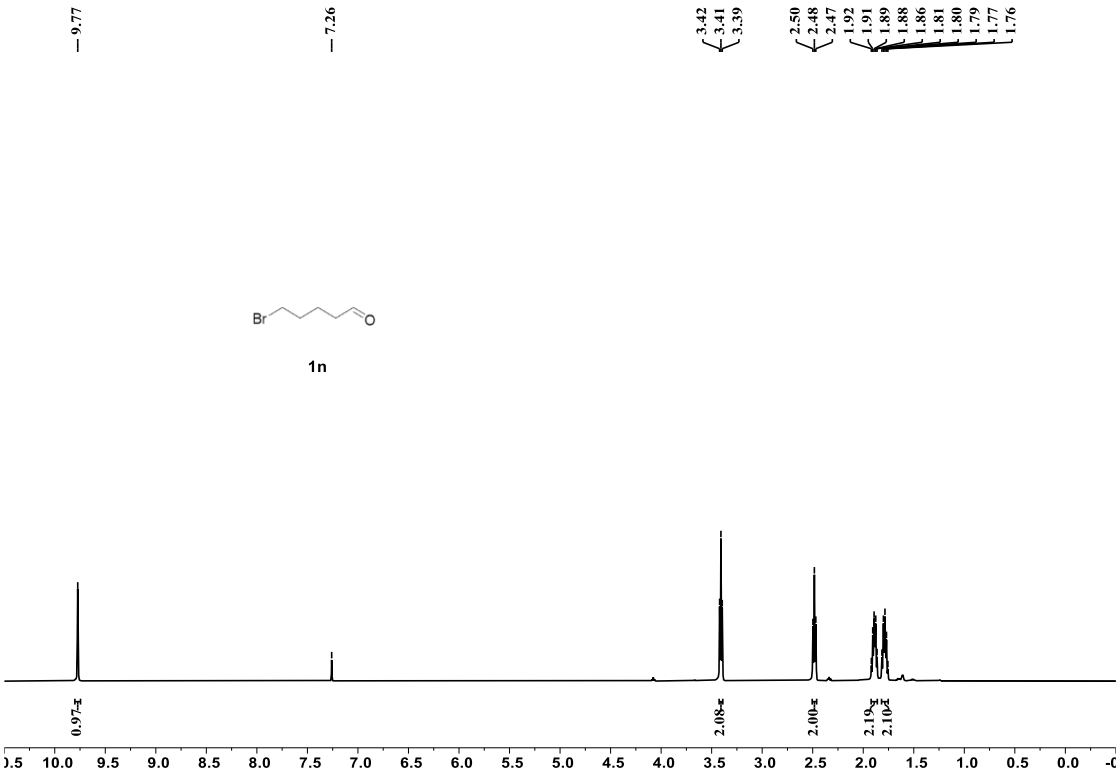
^{1}H NMR (500 MHz, $CDCl_3$)



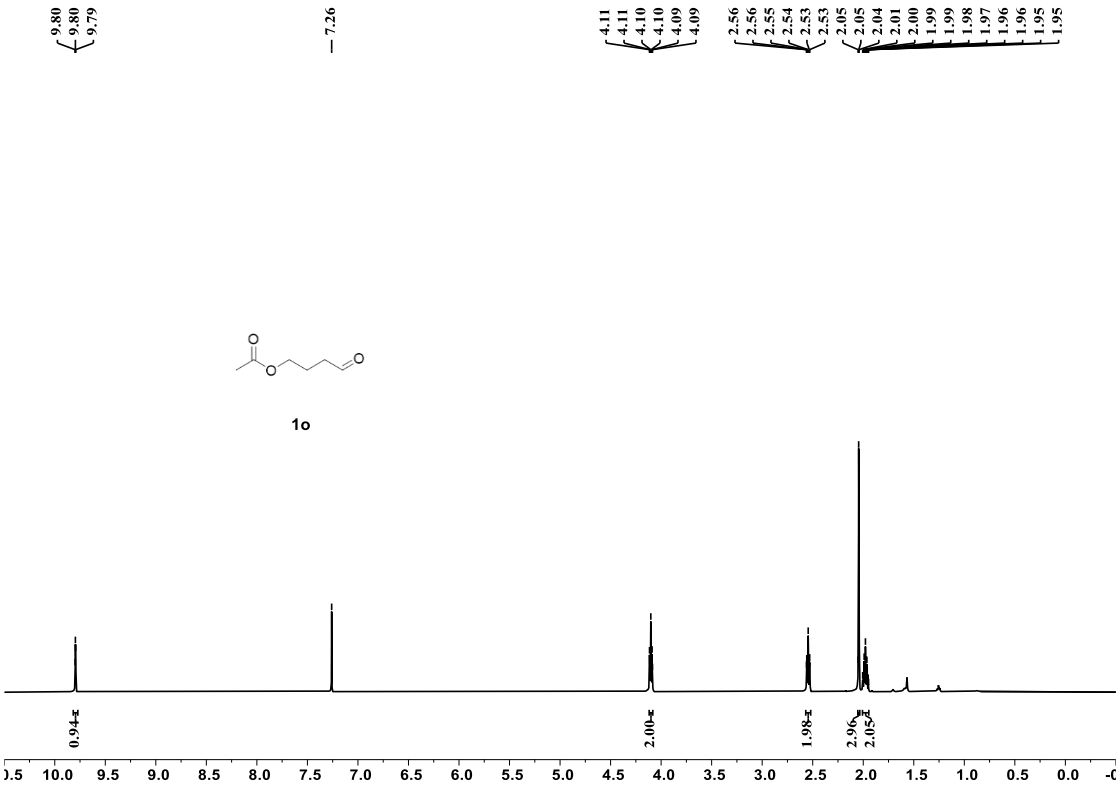
^{13}C NMR (101 MHz, $CDCl_3$)



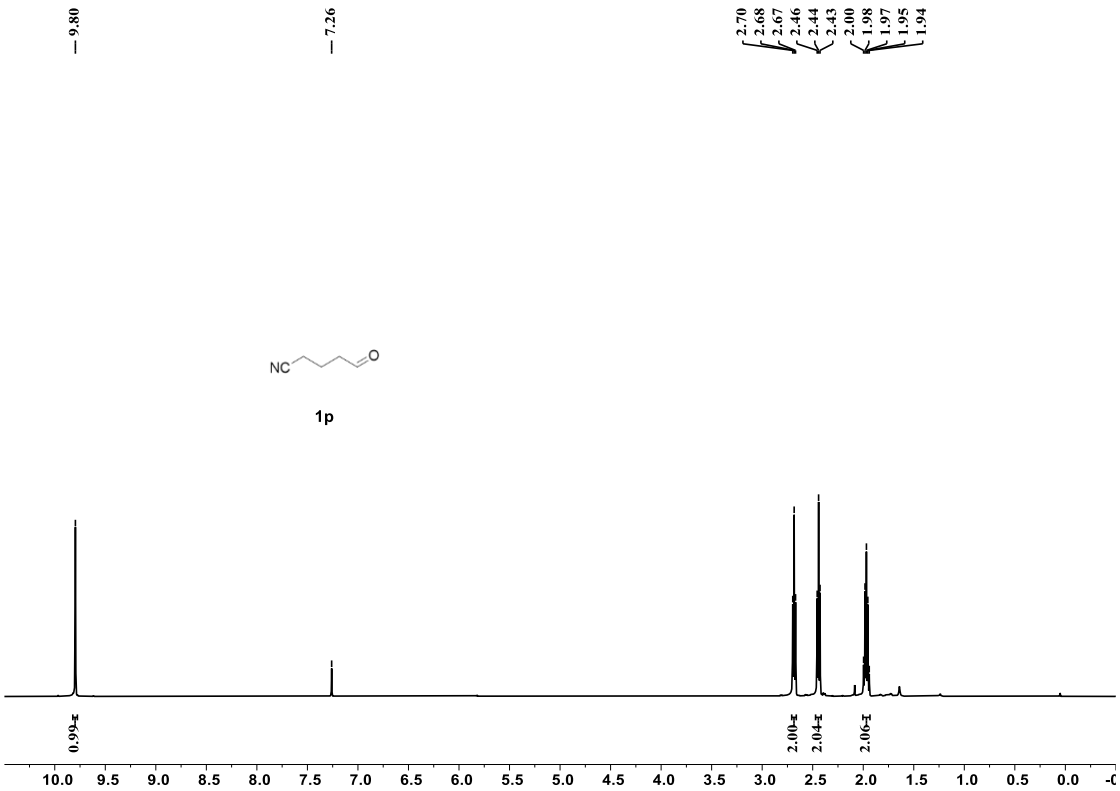
^{1}H NMR (500 MHz, $CDCl_3$)



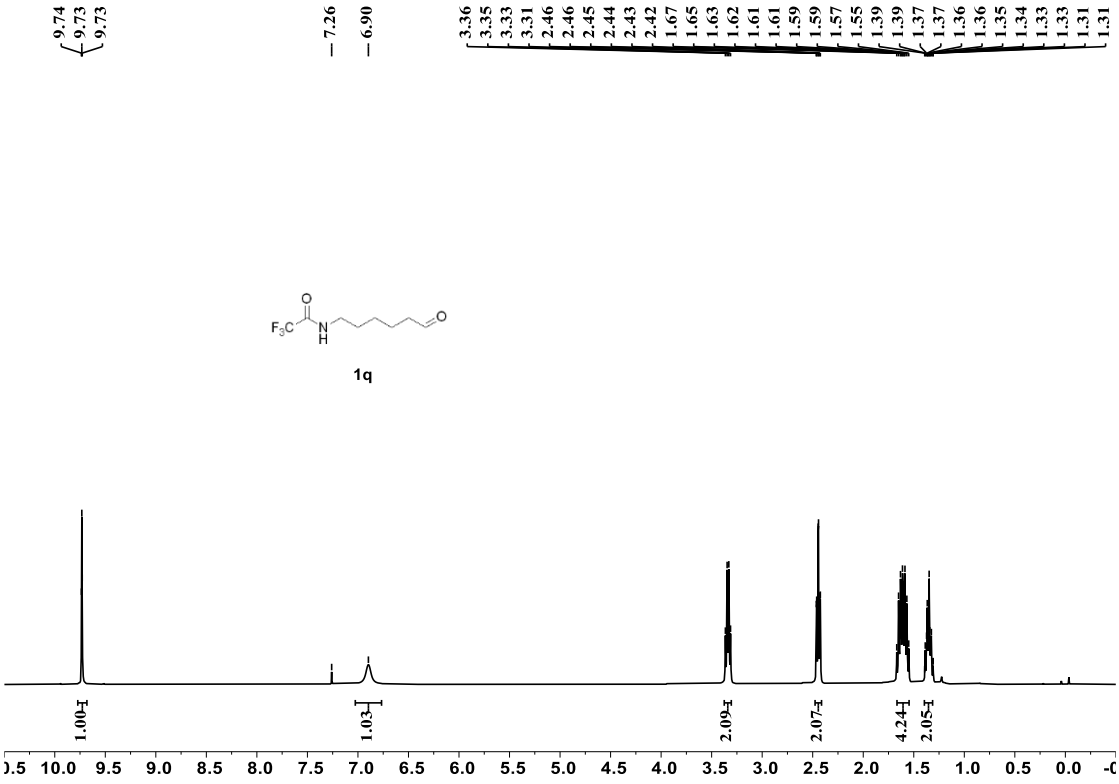
^{1}H NMR (500 MHz, $CDCl_3$)



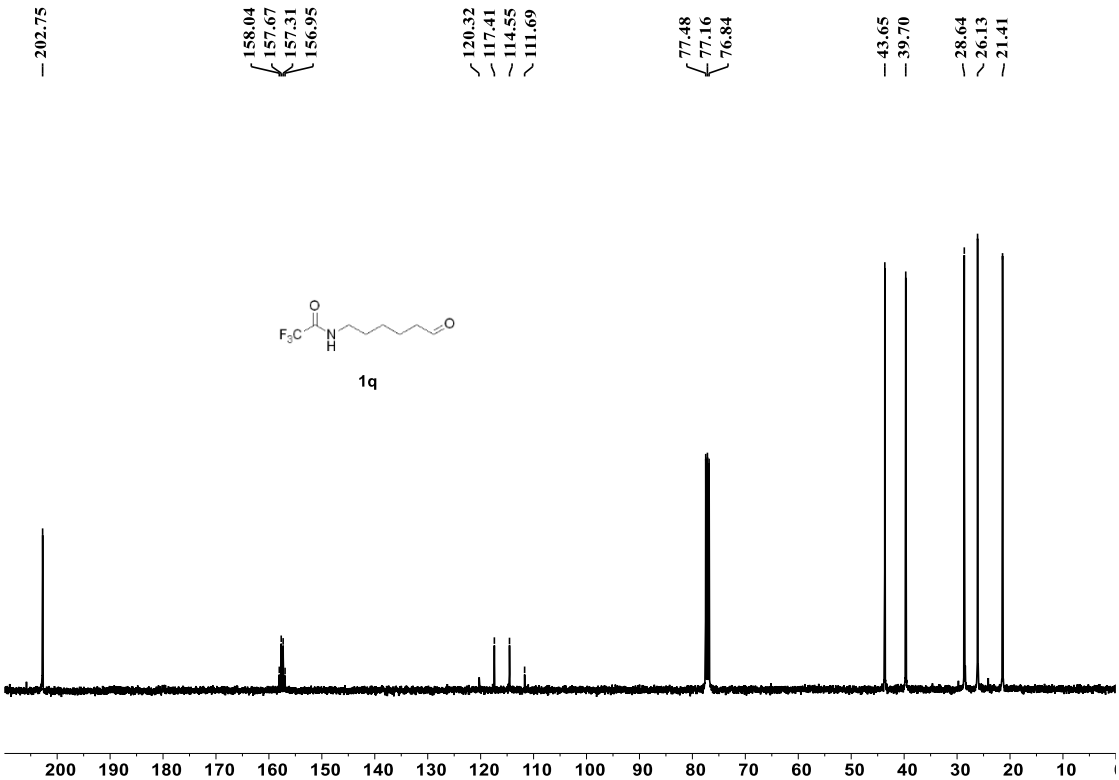
^{1}H NMR (500 MHz, $CDCl_3$)



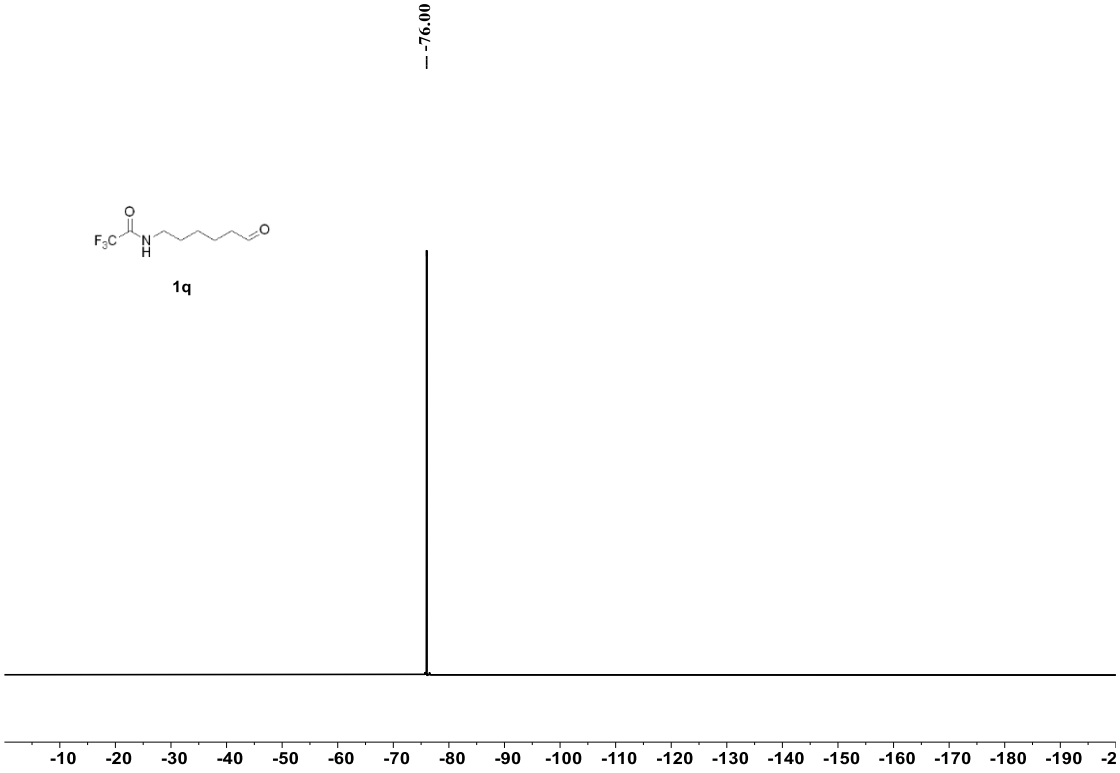
^{1}H NMR (400 MHz, $CDCl_3$)



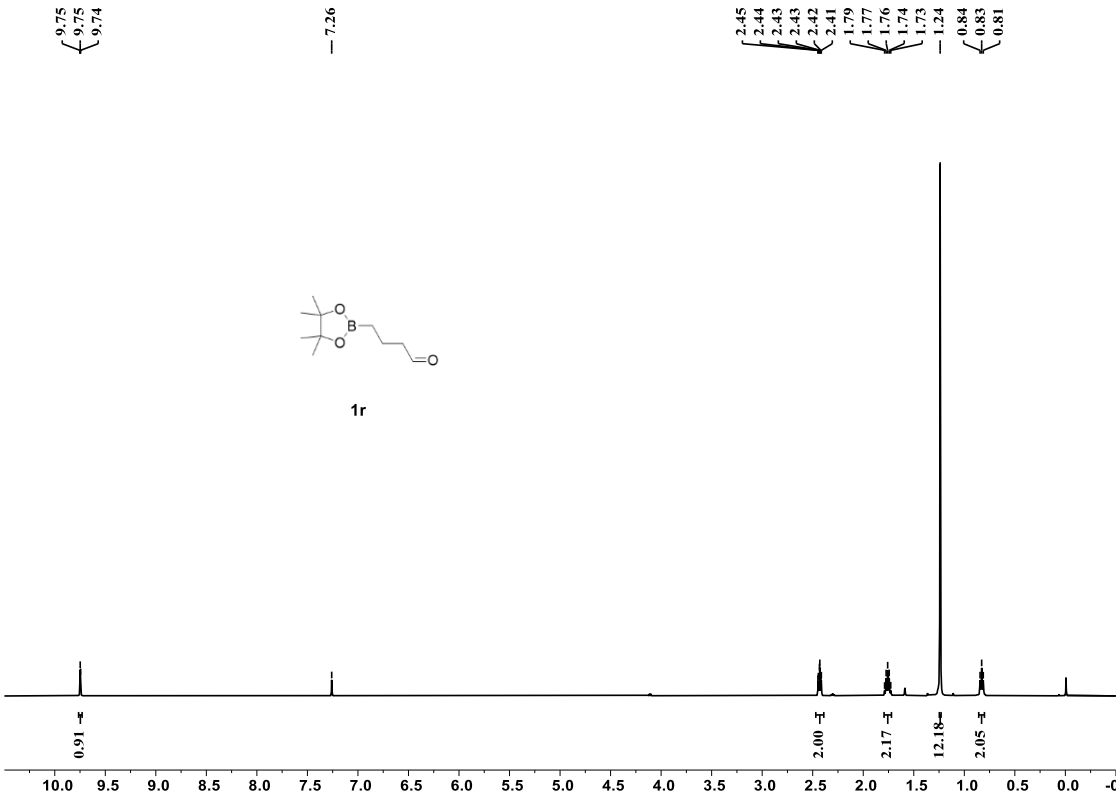
^{13}C NMR (101 MHz, $CDCl_3$)



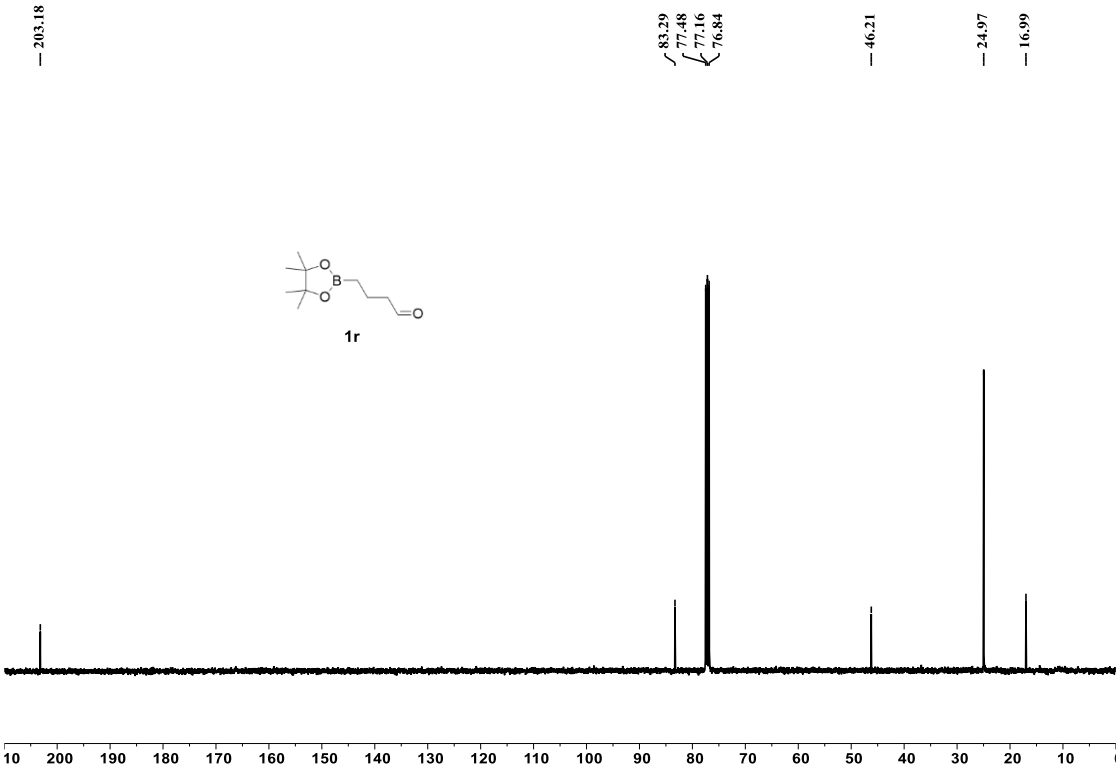
^{19}F NMR (377 MHz, $CDCl_3$)



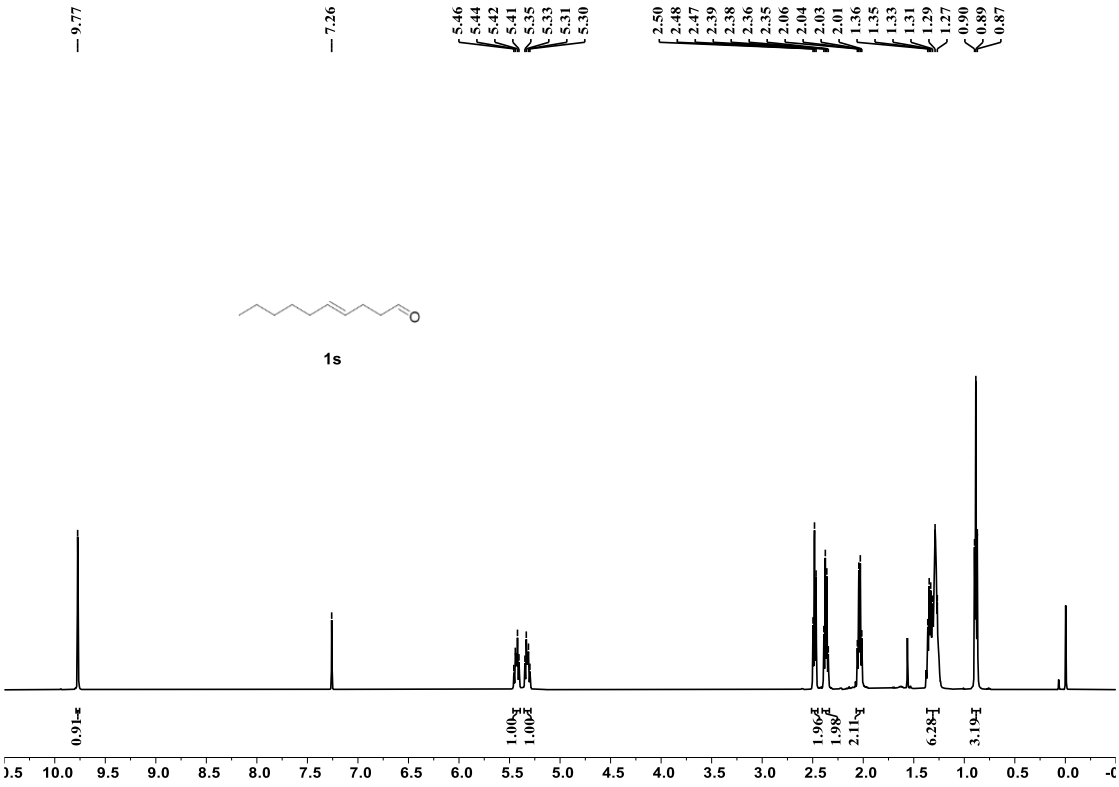
^{1}H NMR (500 MHz, $CDCl_3$)



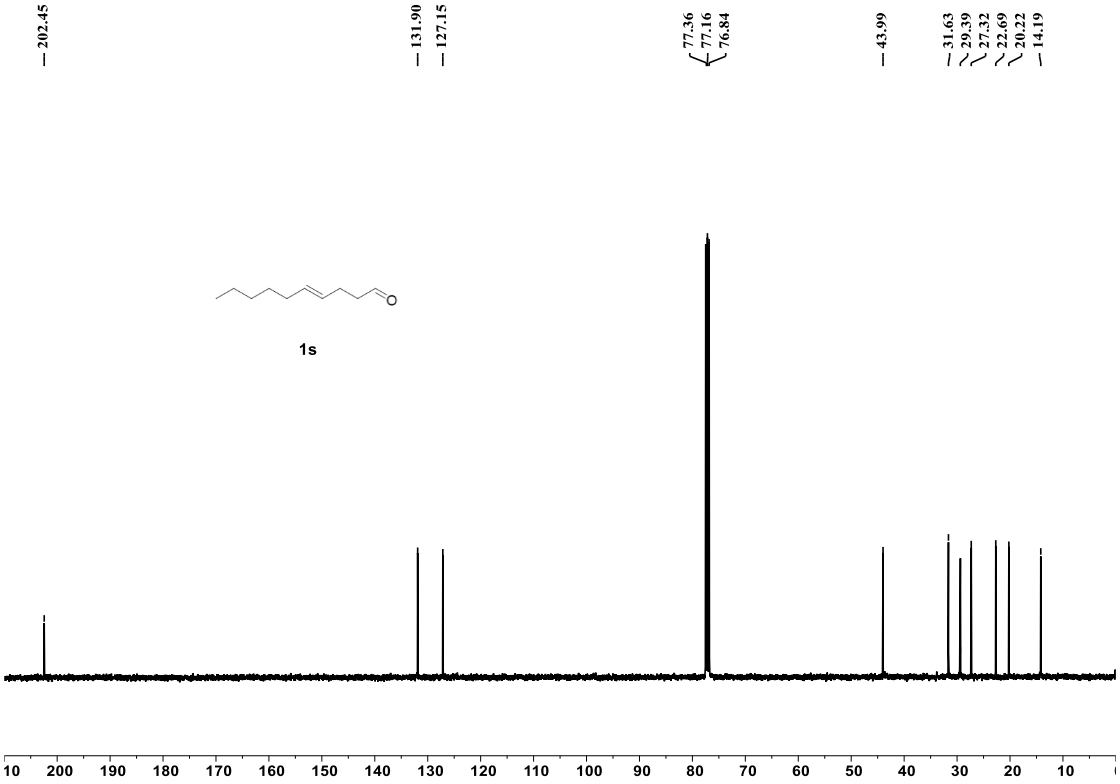
^{13}C NMR (101 MHz, $CDCl_3$)



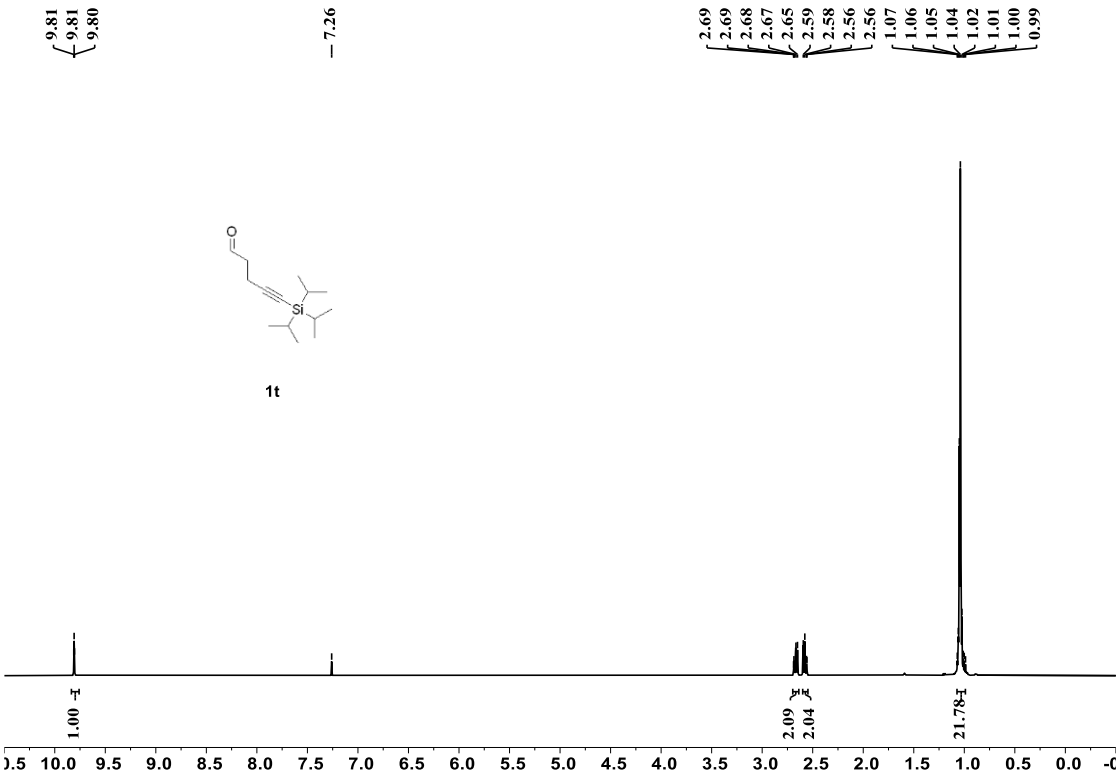
^{1}H NMR (500 MHz, $CDCl_3$)



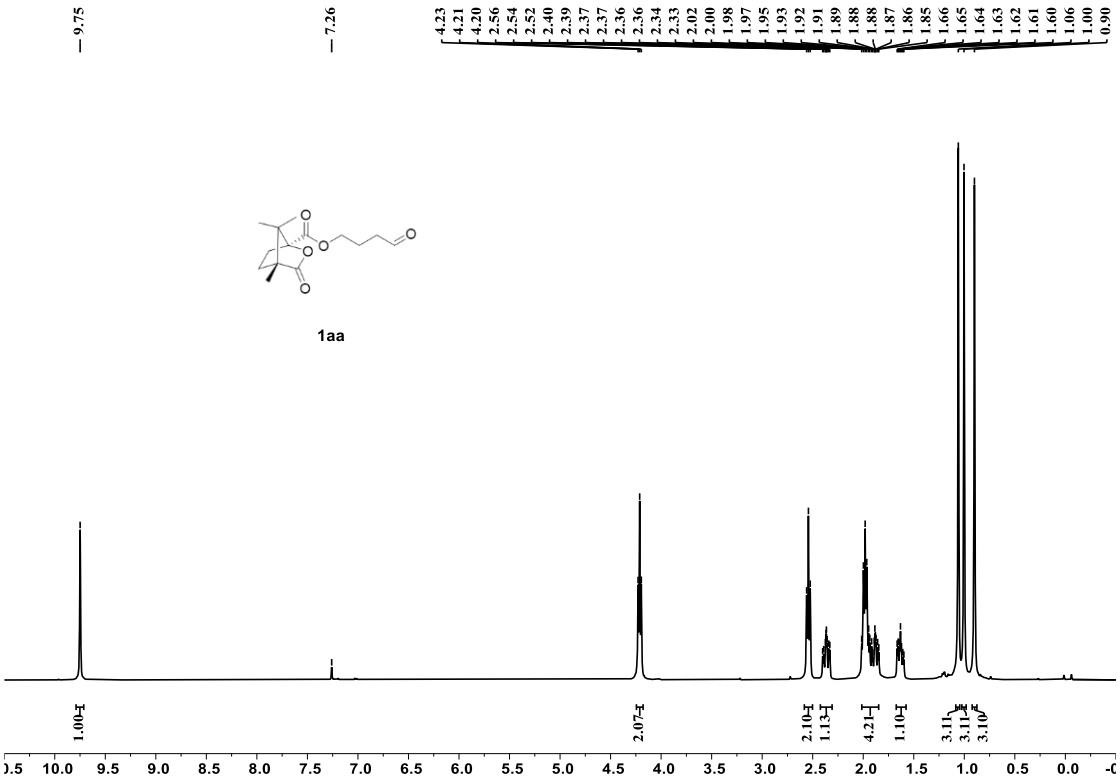
^{13}C NMR (101 MHz, $CDCl_3$)



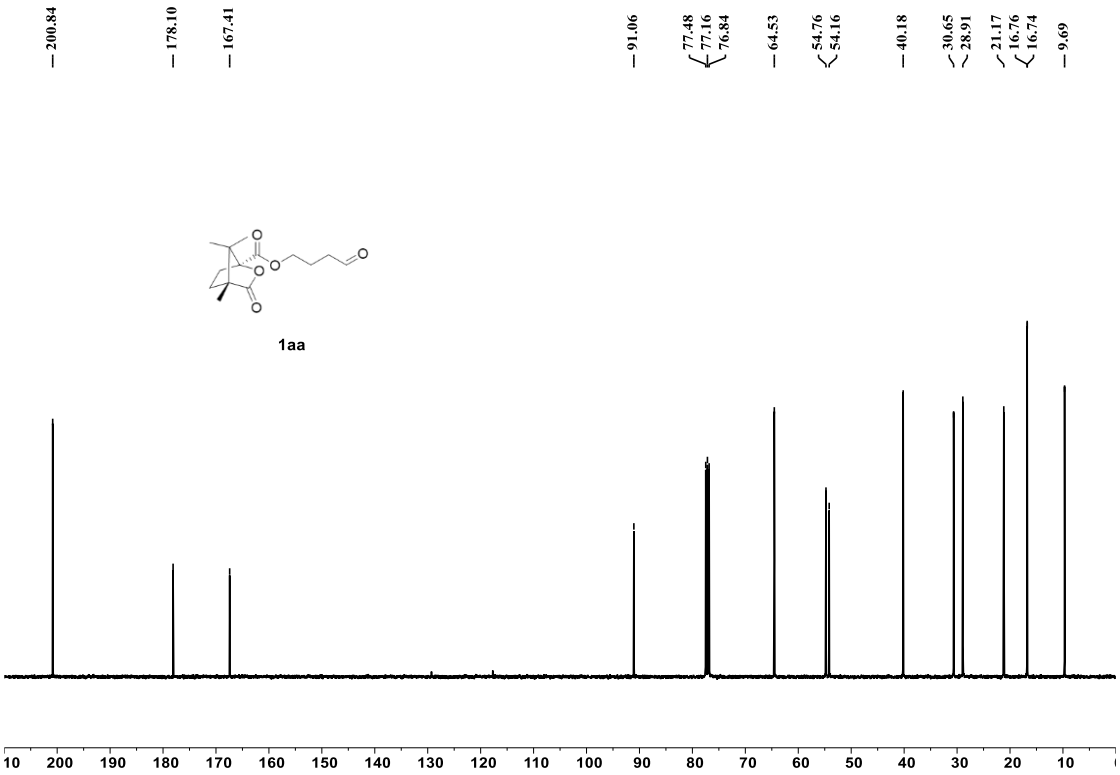
^{1}H NMR (400 MHz, $CDCl_3$)



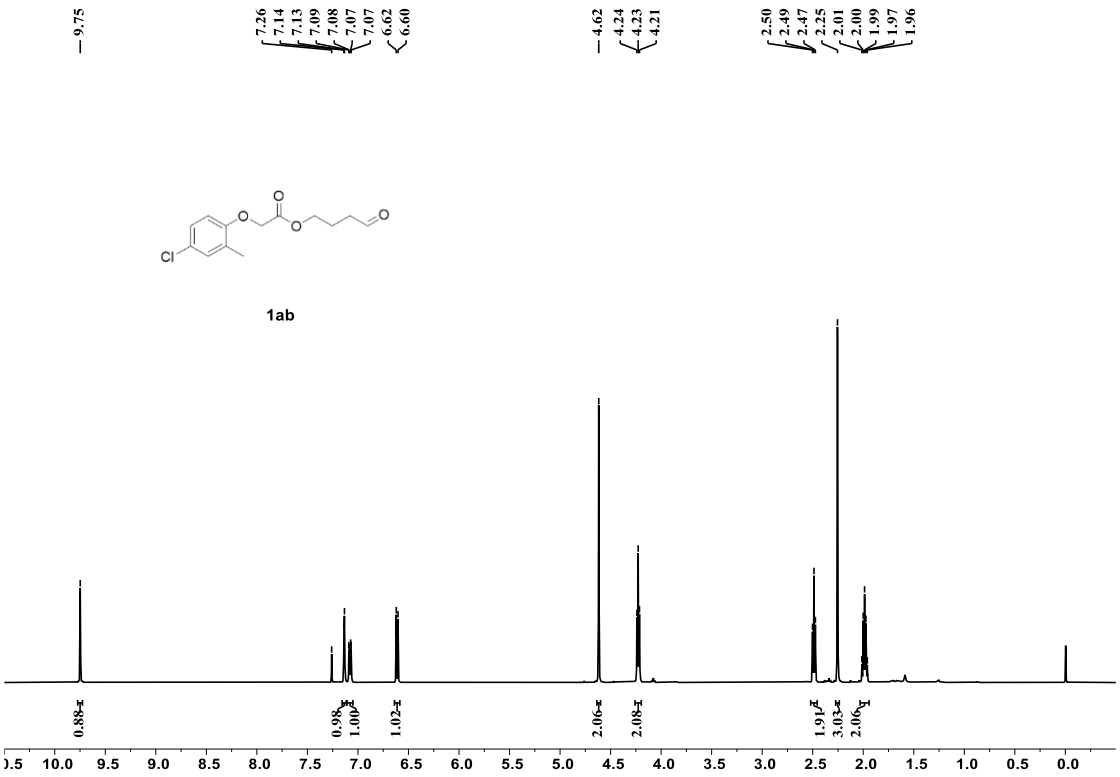
^{1}H NMR (400 MHz, $CDCl_3$)



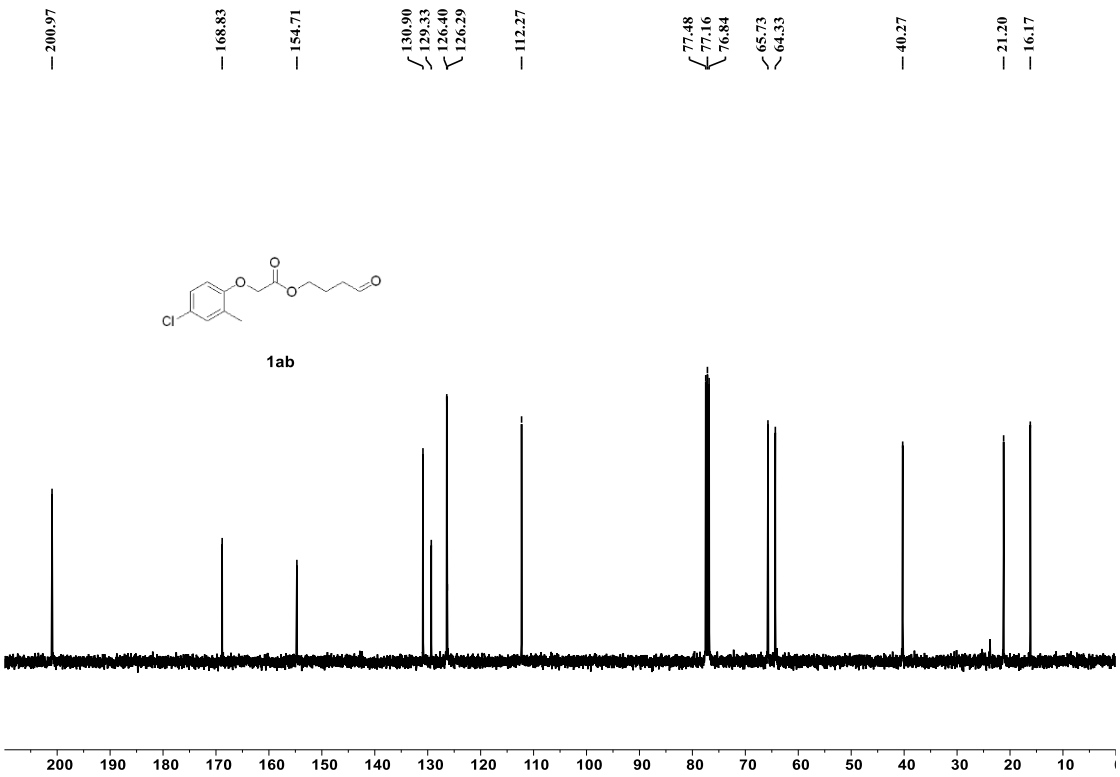
^{13}C NMR (101 MHz, $CDCl_3$)



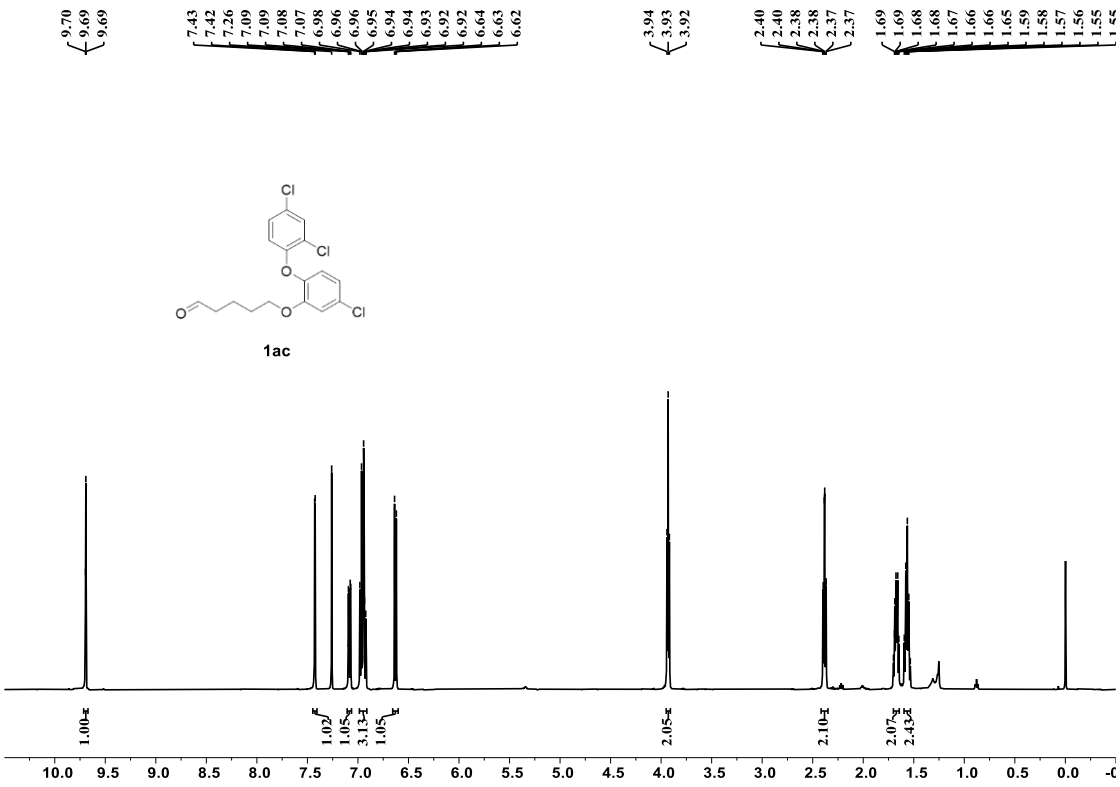
^{1}H NMR (500 MHz, $CDCl_3$)



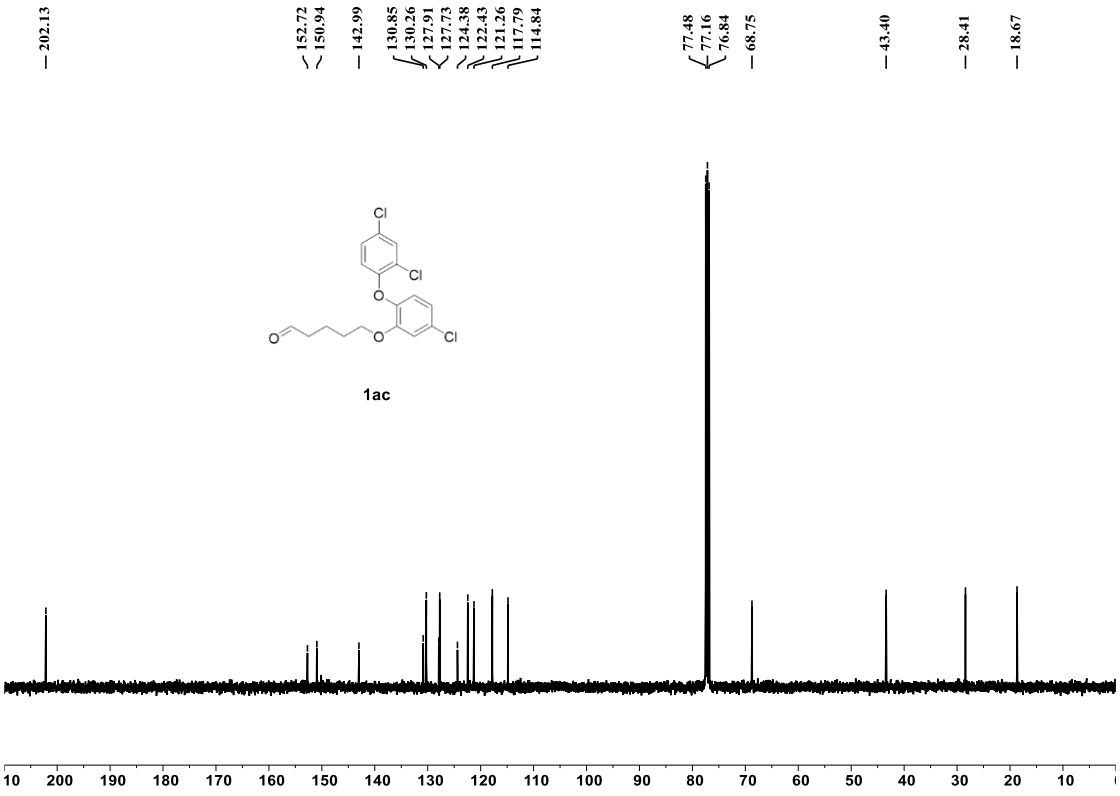
^{13}C NMR (101 MHz, $CDCl_3$)



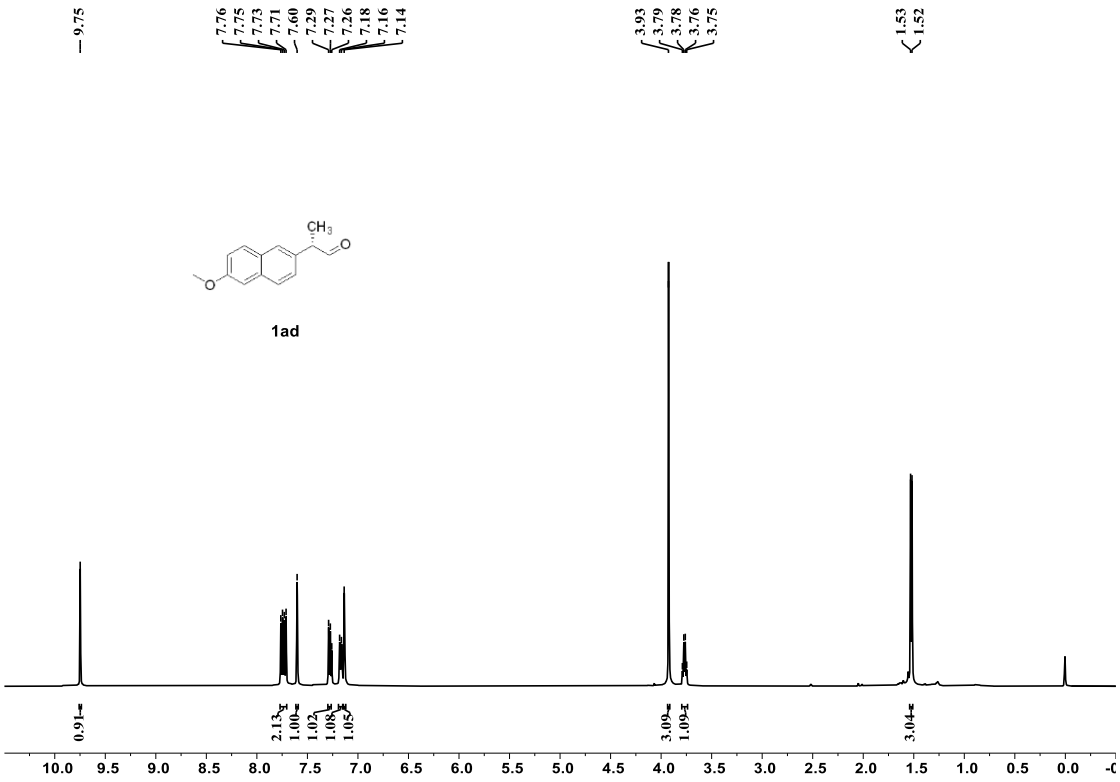
^{1}H NMR (400 MHz, $CDCl_3$)



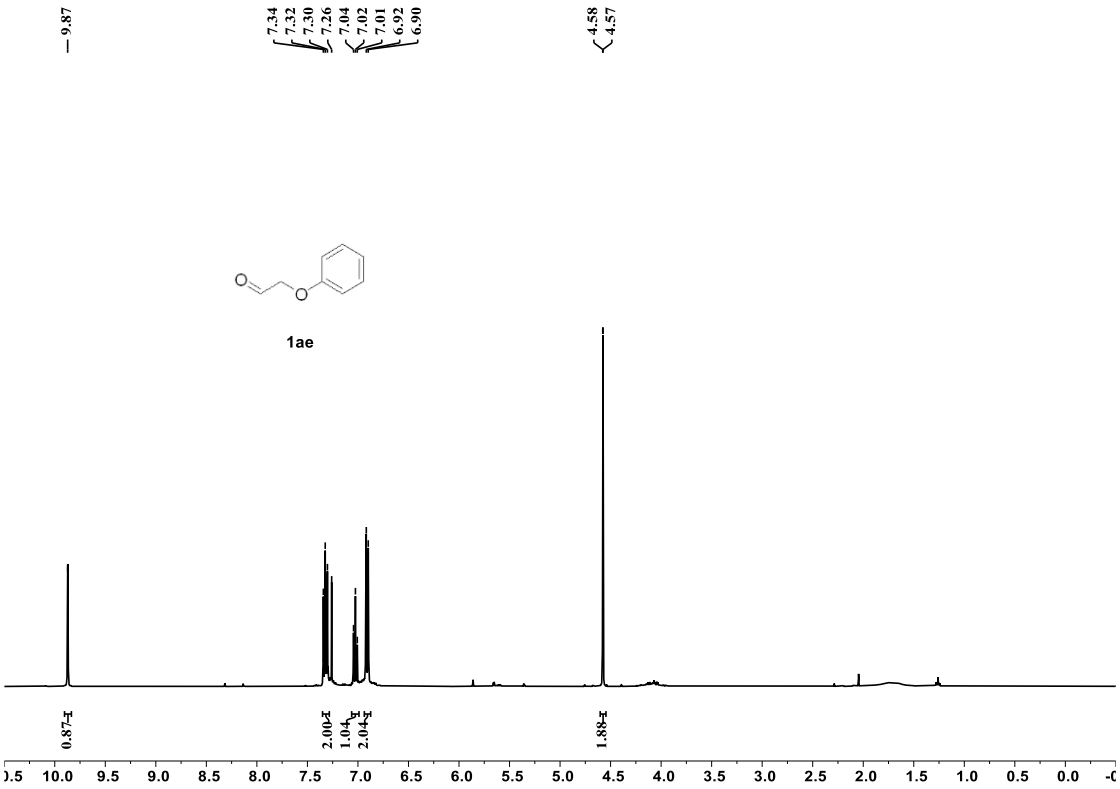
^{13}C NMR (101 MHz, $CDCl_3$)



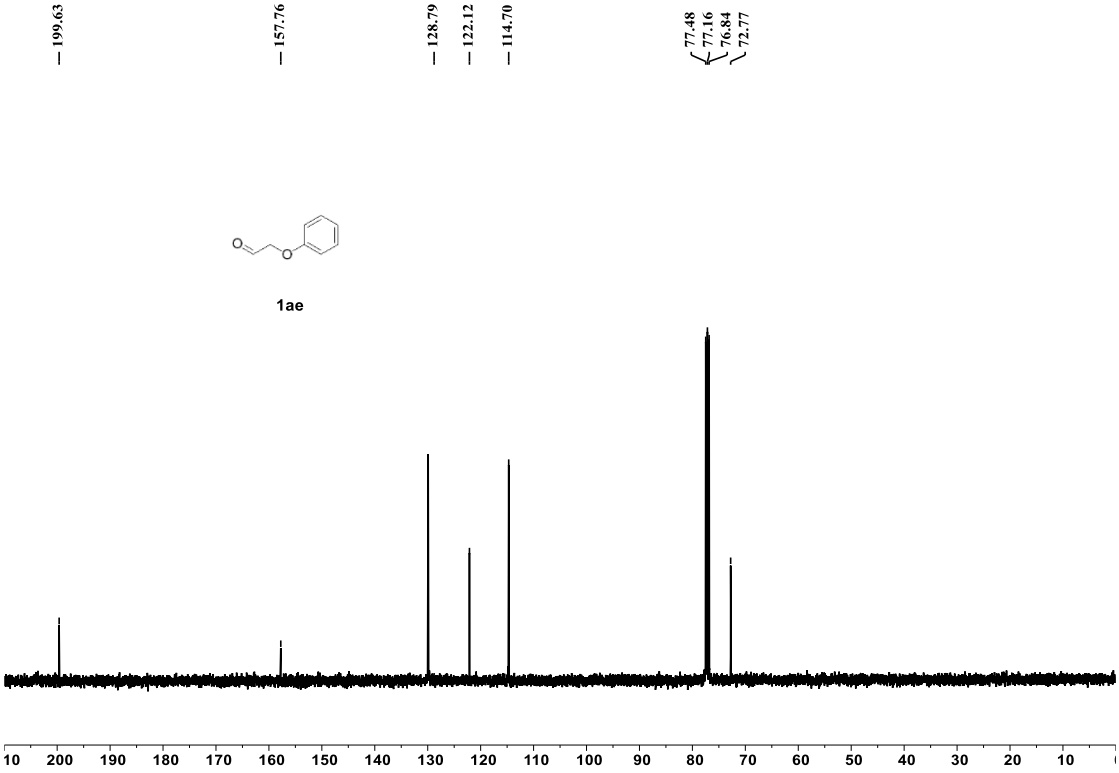
^{1}H NMR (500 MHz, $CDCl_3$)



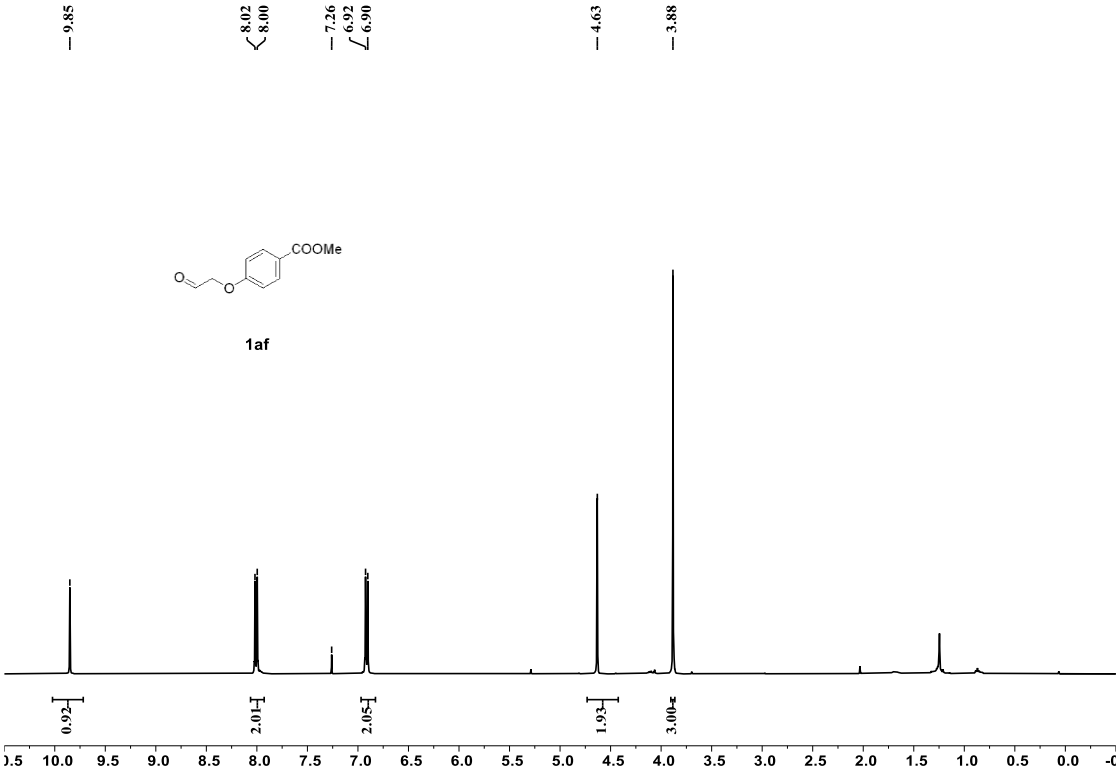
^{1}H NMR (400 MHz, $CDCl_3$)



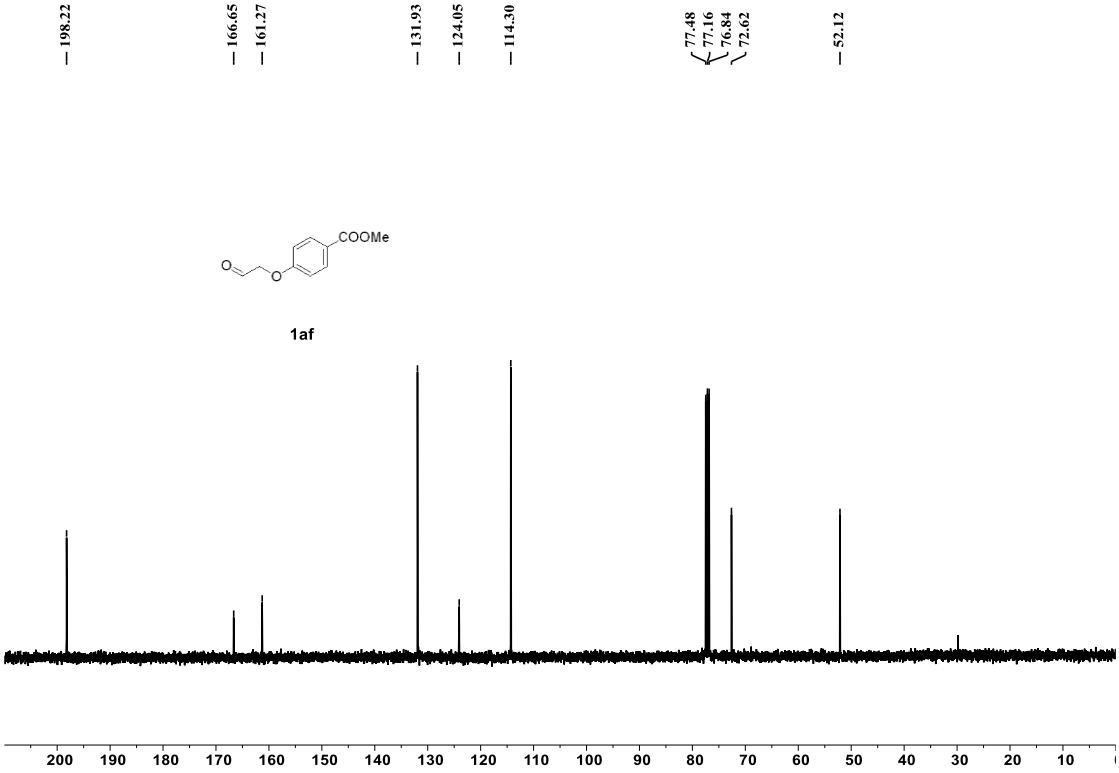
^{13}C NMR (101 MHz, $CDCl_3$)



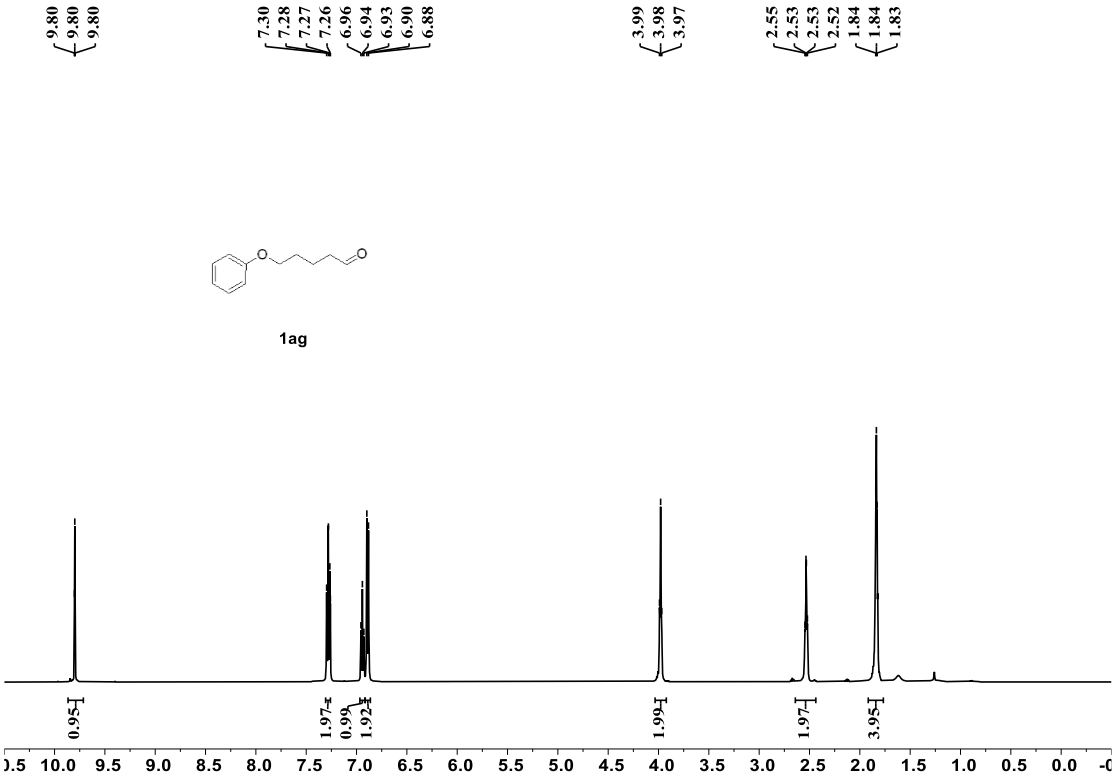
^{1}H NMR (400 MHz, $CDCl_3$)



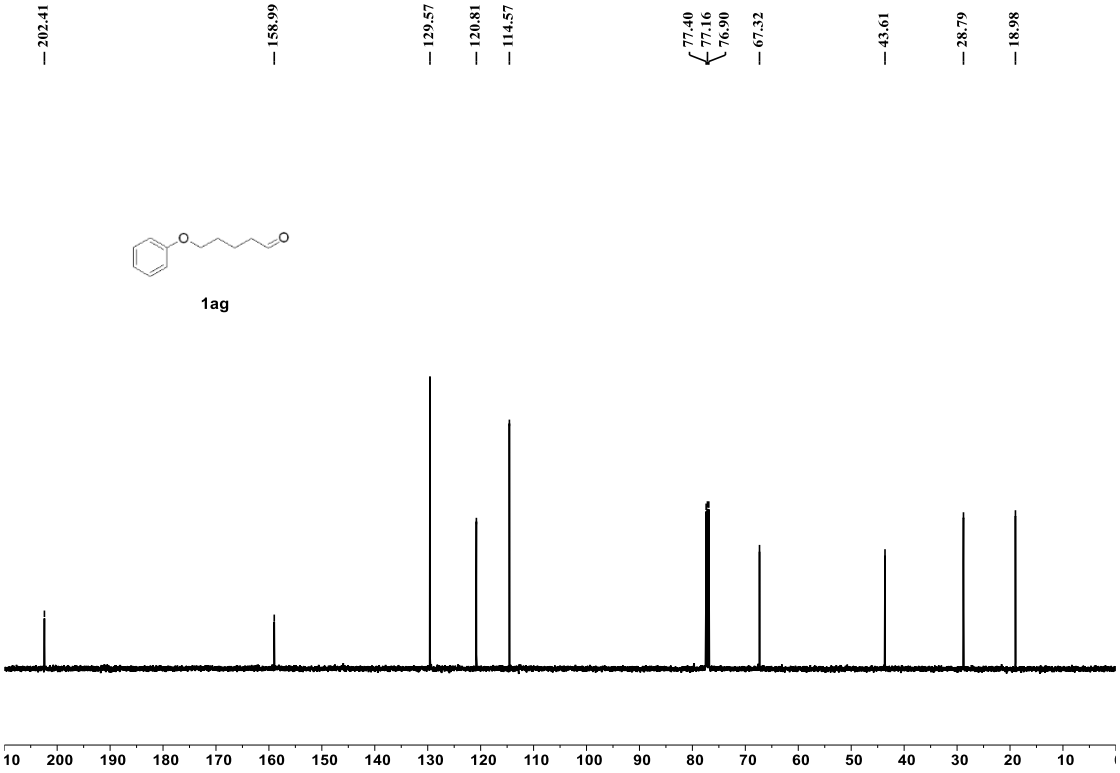
^{13}C NMR (101 MHz, $CDCl_3$)



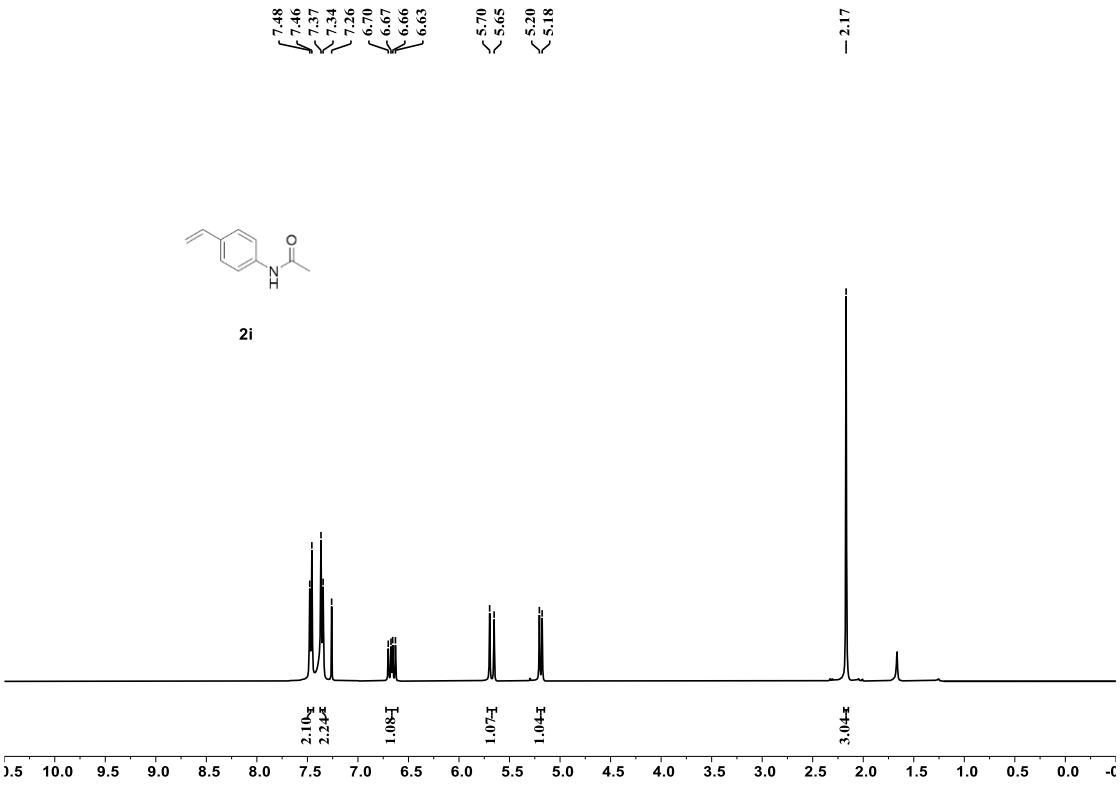
^{1}H NMR (500 MHz, $CDCl_3$)



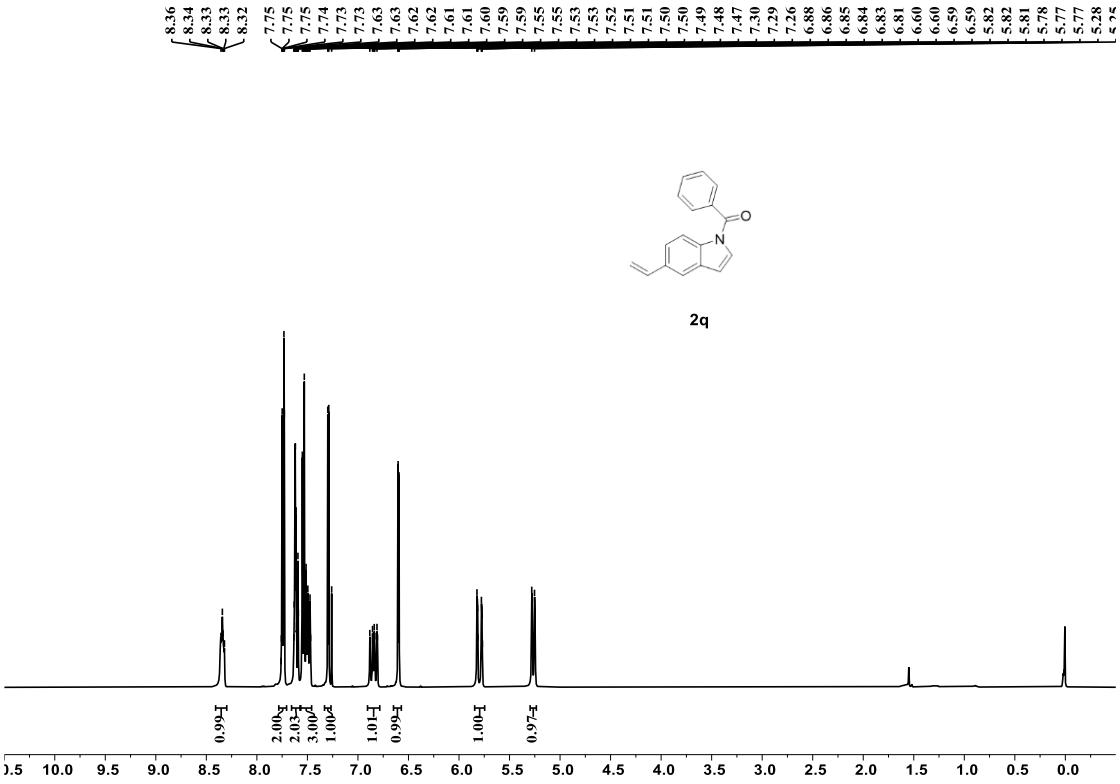
^{13}C NMR (126 MHz, $CDCl_3$)



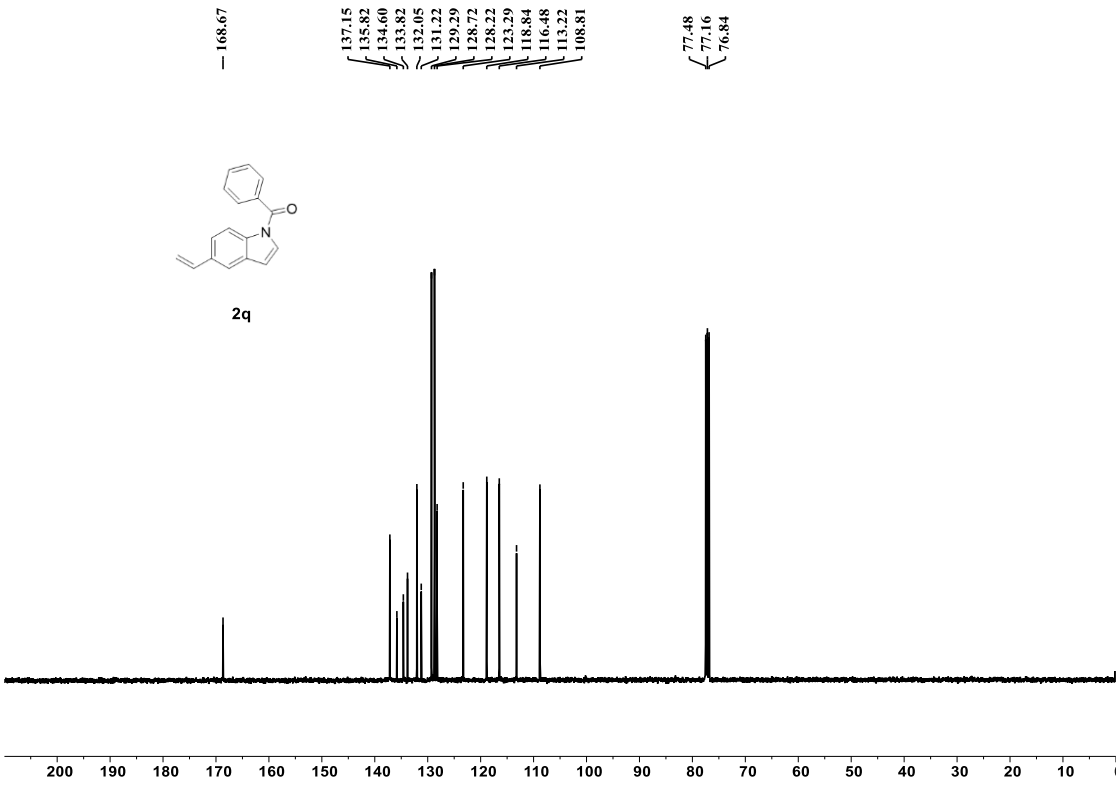
^{1}H NMR (400 MHz, $CDCl_3$)



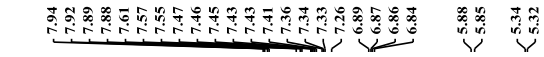
^{1}H NMR (500 MHz, $CDCl_3$)

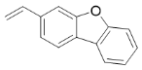


^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)





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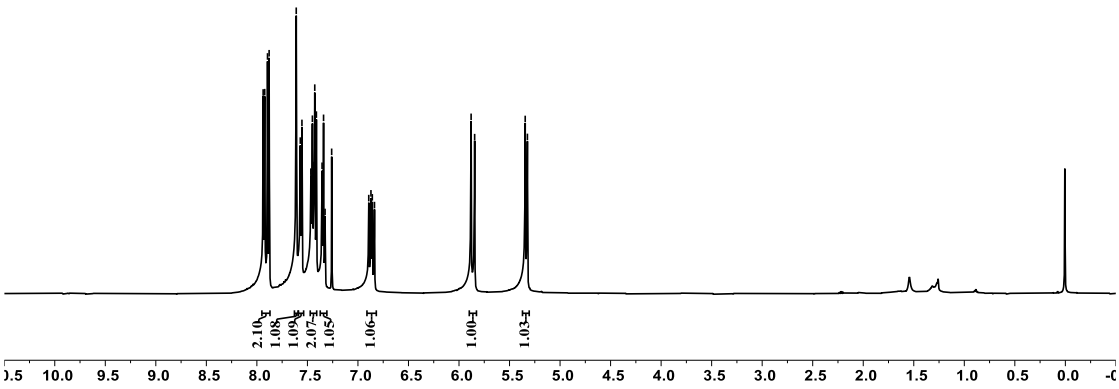
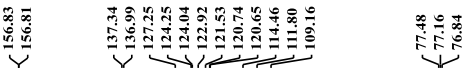
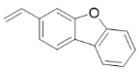


^{13}C NMR (101 MHz, $CDCl_3$)





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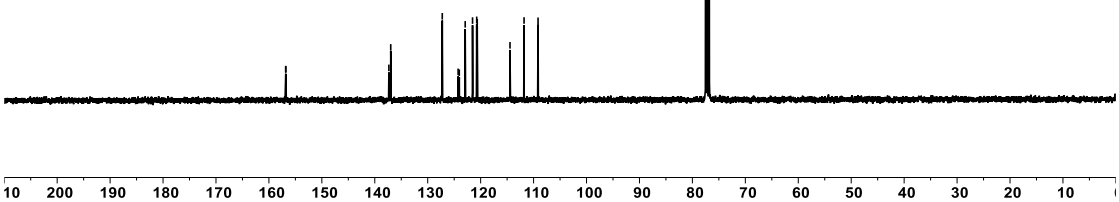
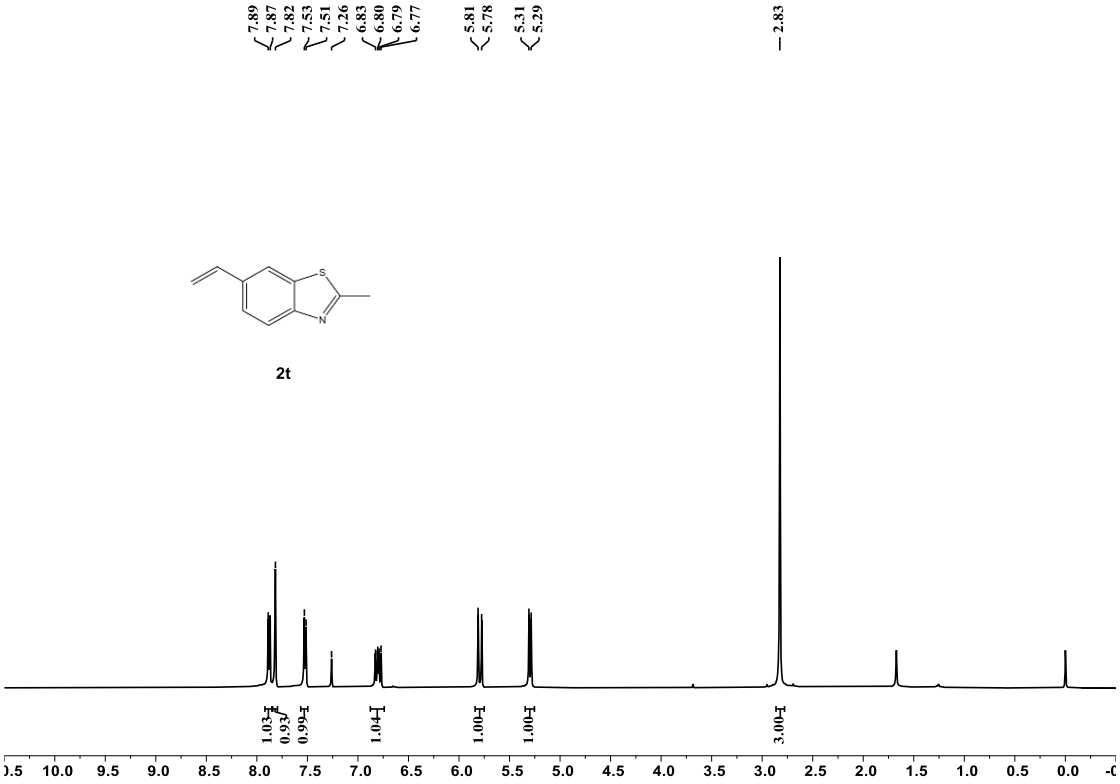
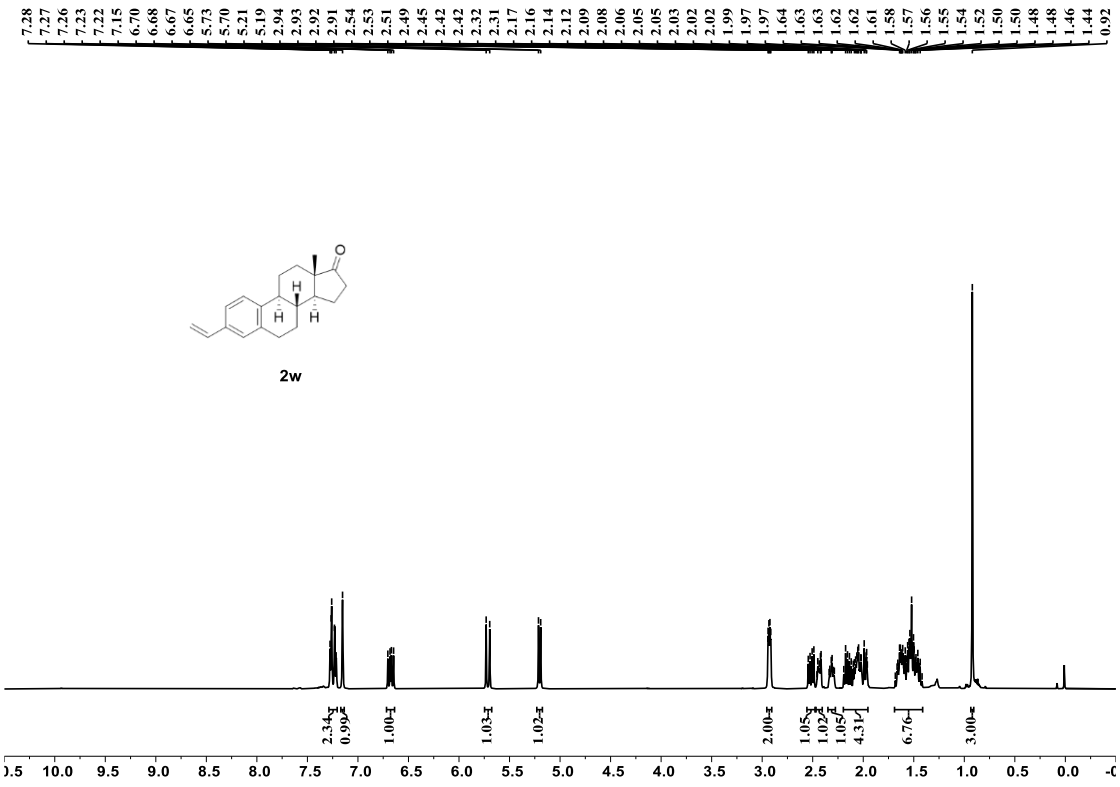


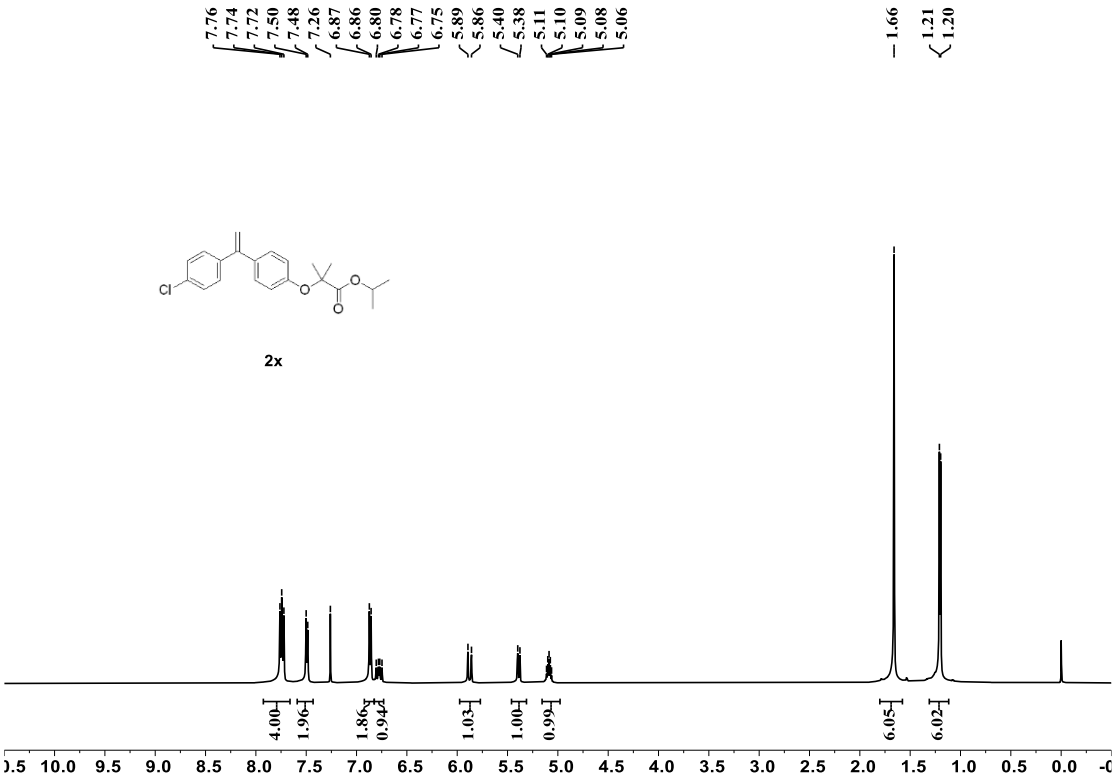
^{1}H NMR (500 MHz, $CDCl_3$)



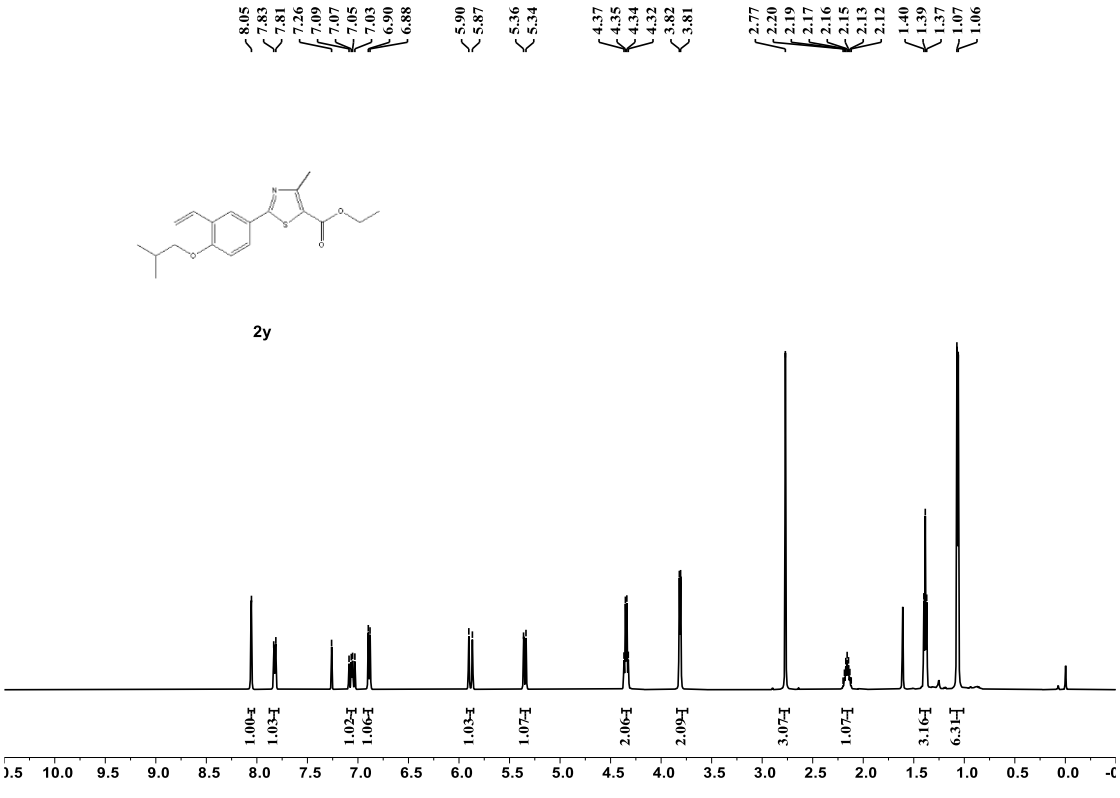
^{1}H NMR (500 MHz, $CDCl_3$)



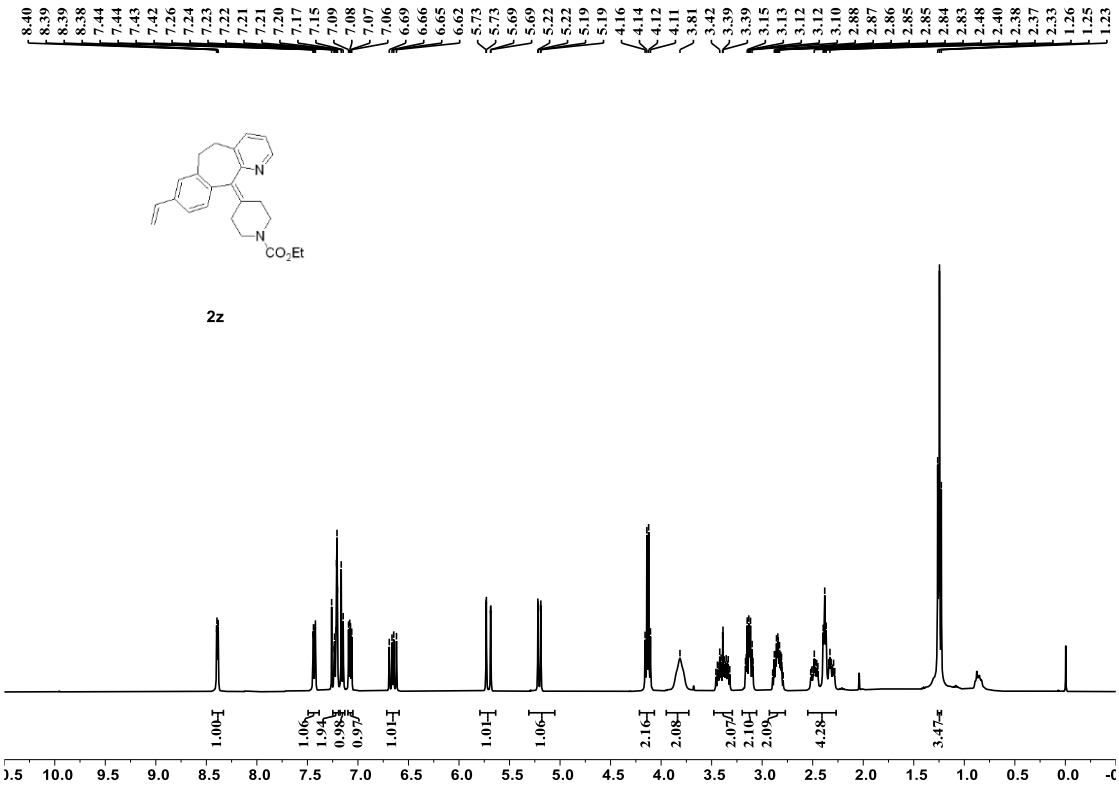
^{1}H NMR (500 MHz, $CDCl_3$)



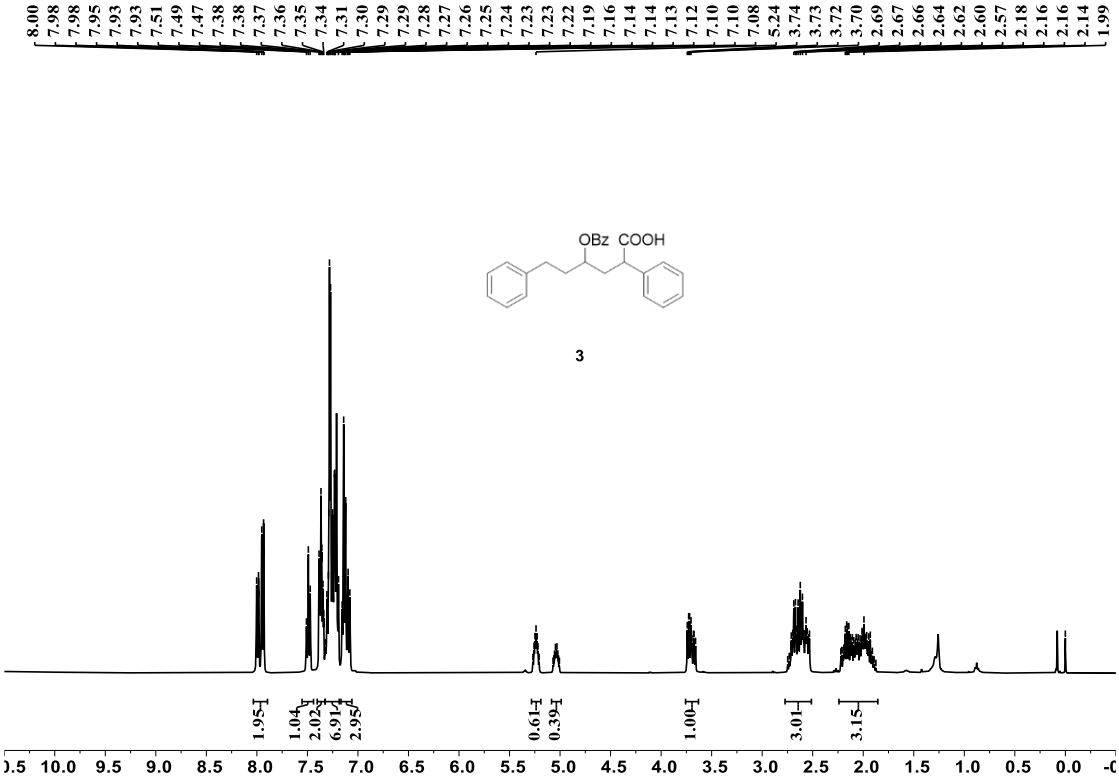
^{1}H NMR (500 MHz, $CDCl_3$)



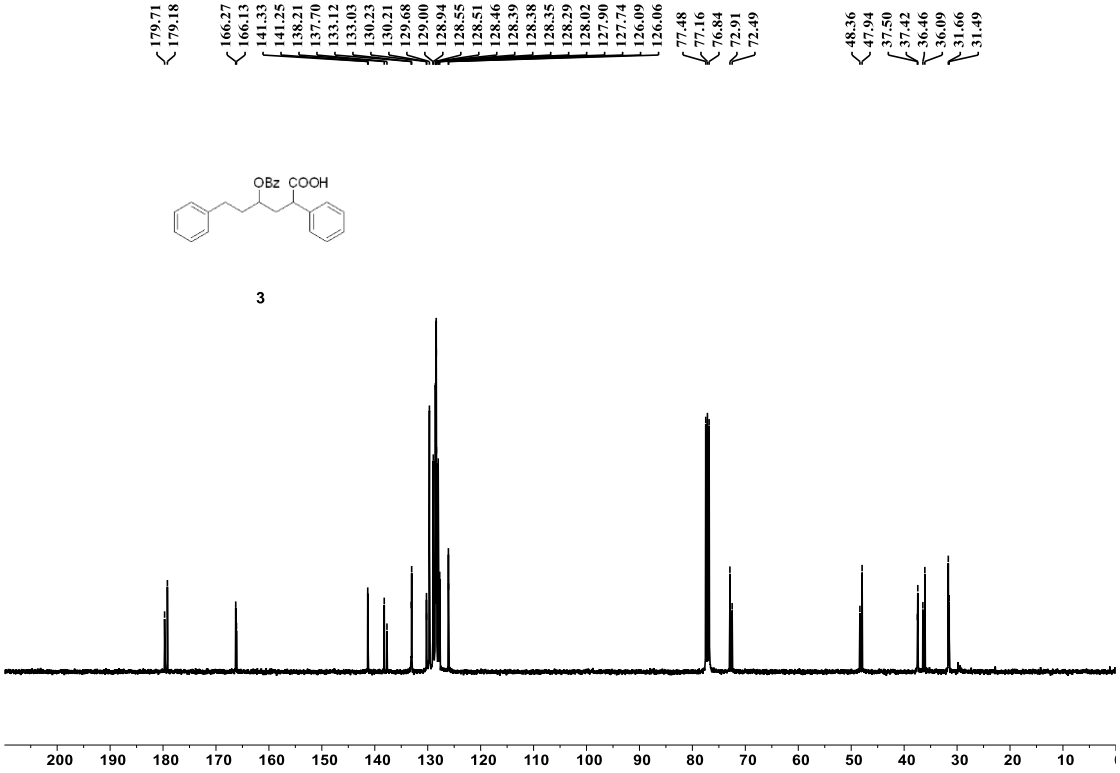
^{1}H NMR (400 MHz, $CDCl_3$)



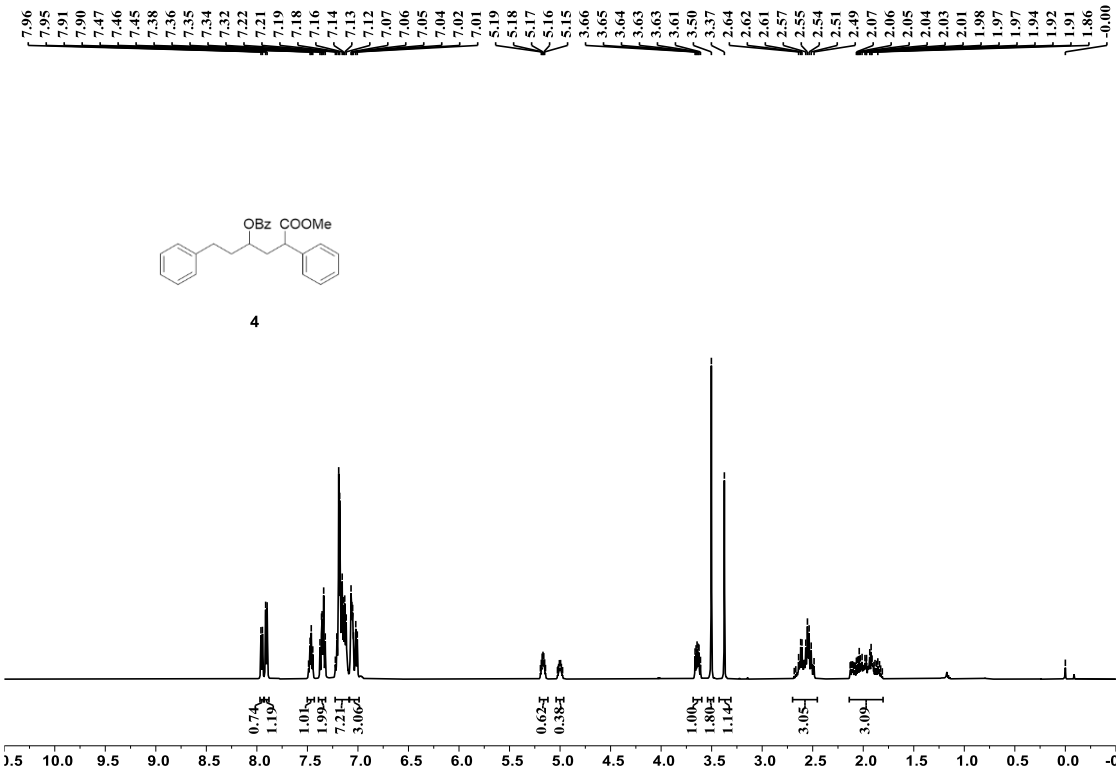
^{1}H NMR (400 MHz, $CDCl_3$)



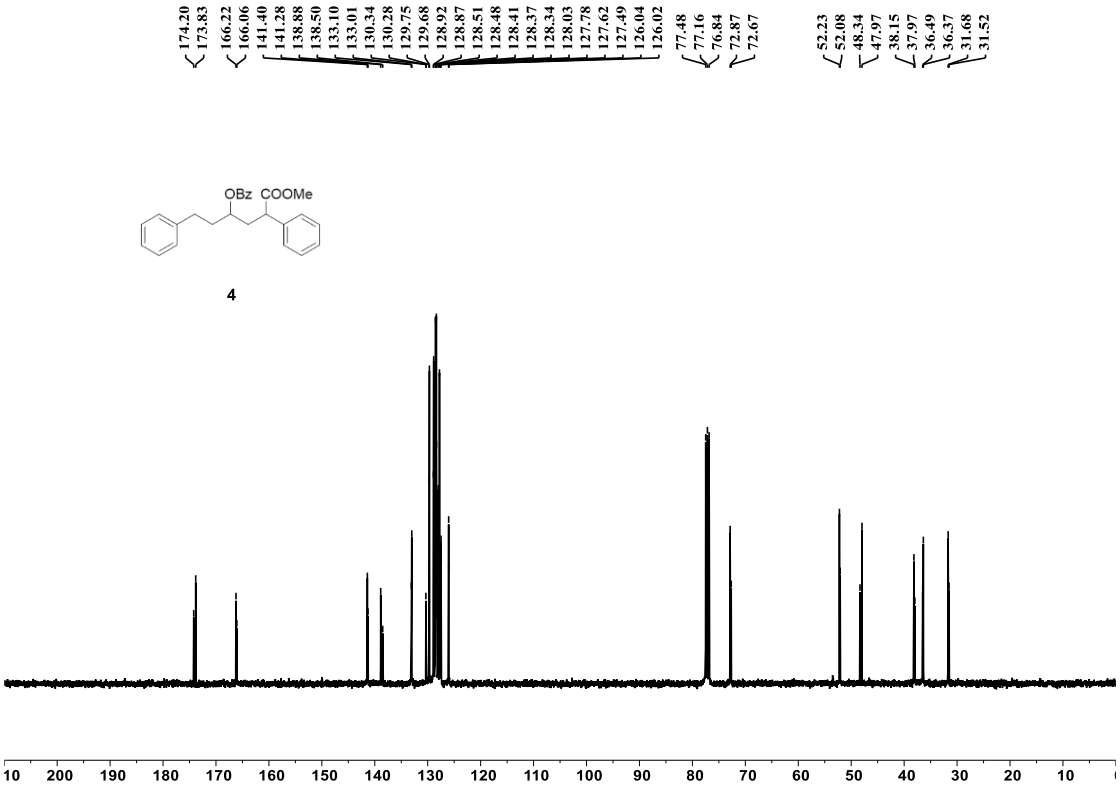
^{13}C NMR (101 MHz, $CDCl_3$)



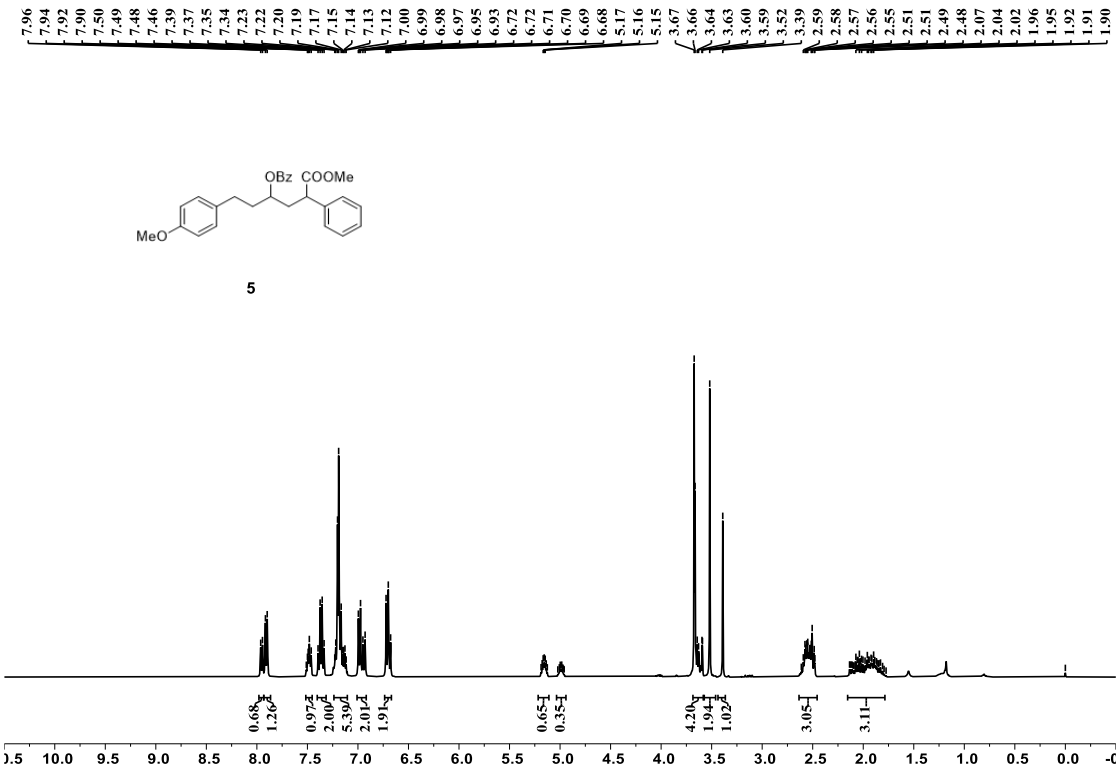
^{1}H NMR (500 MHz, $CDCl_3$)



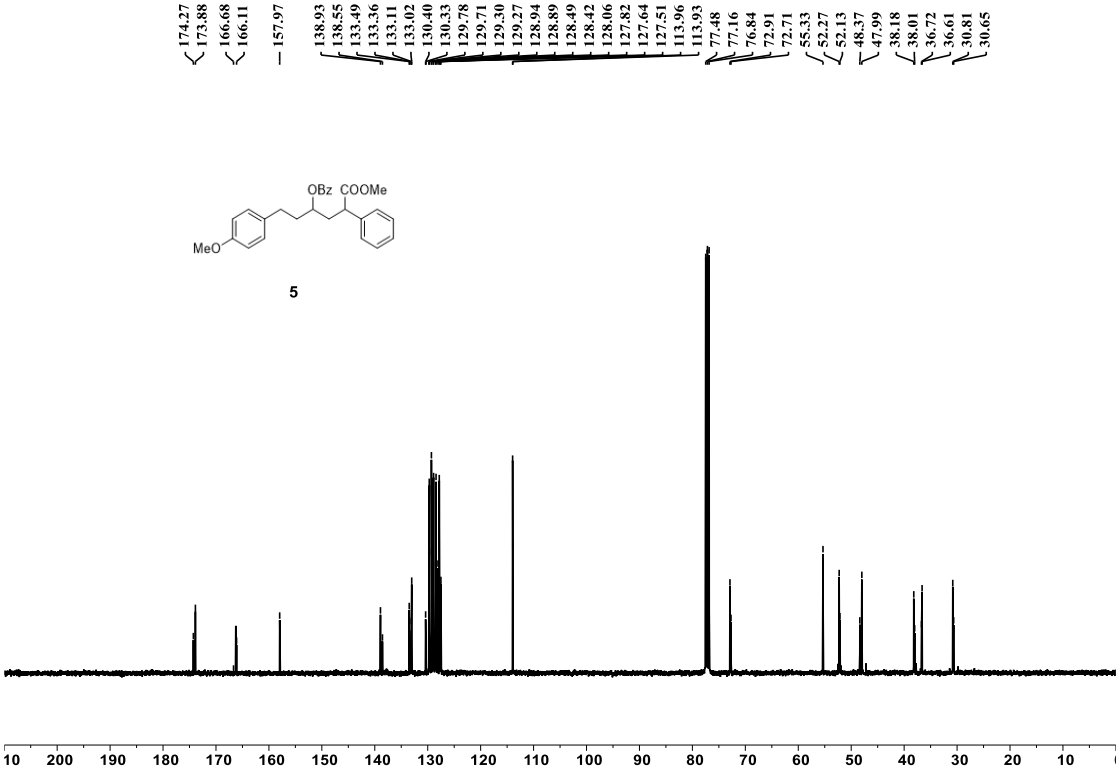
^{13}C NMR (101 MHz, $CDCl_3$)



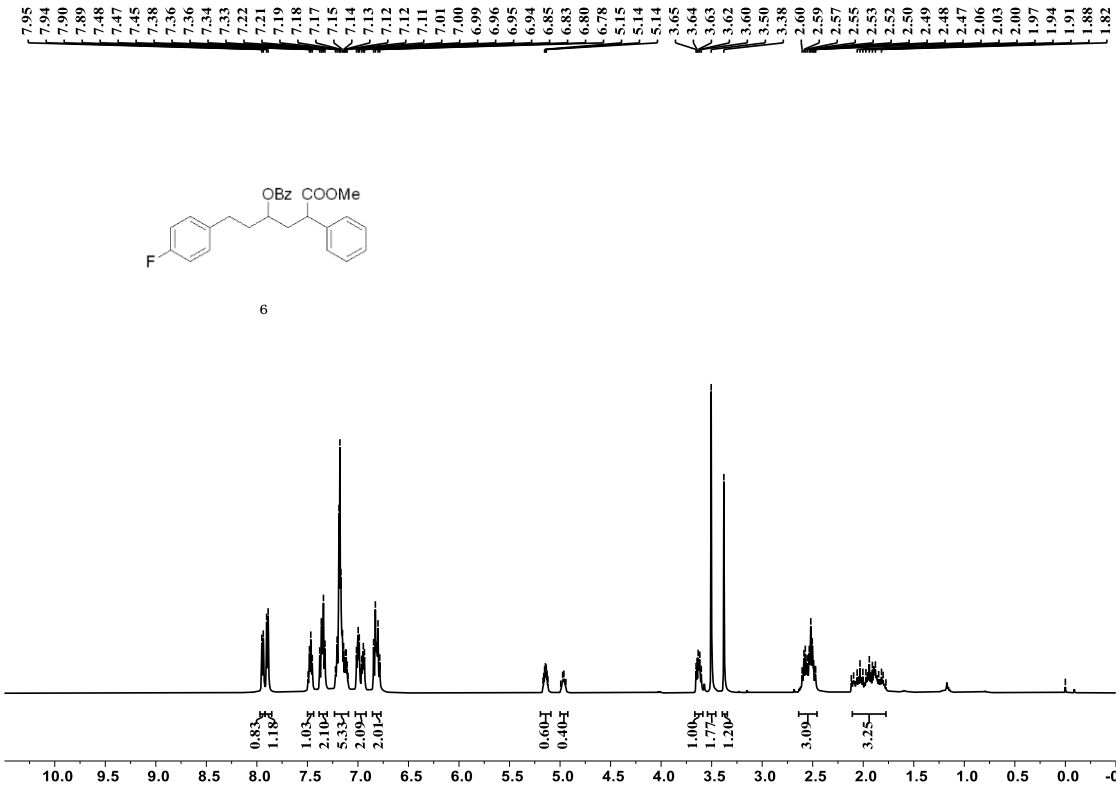
^{1}H NMR (400 MHz, $CDCl_3$)



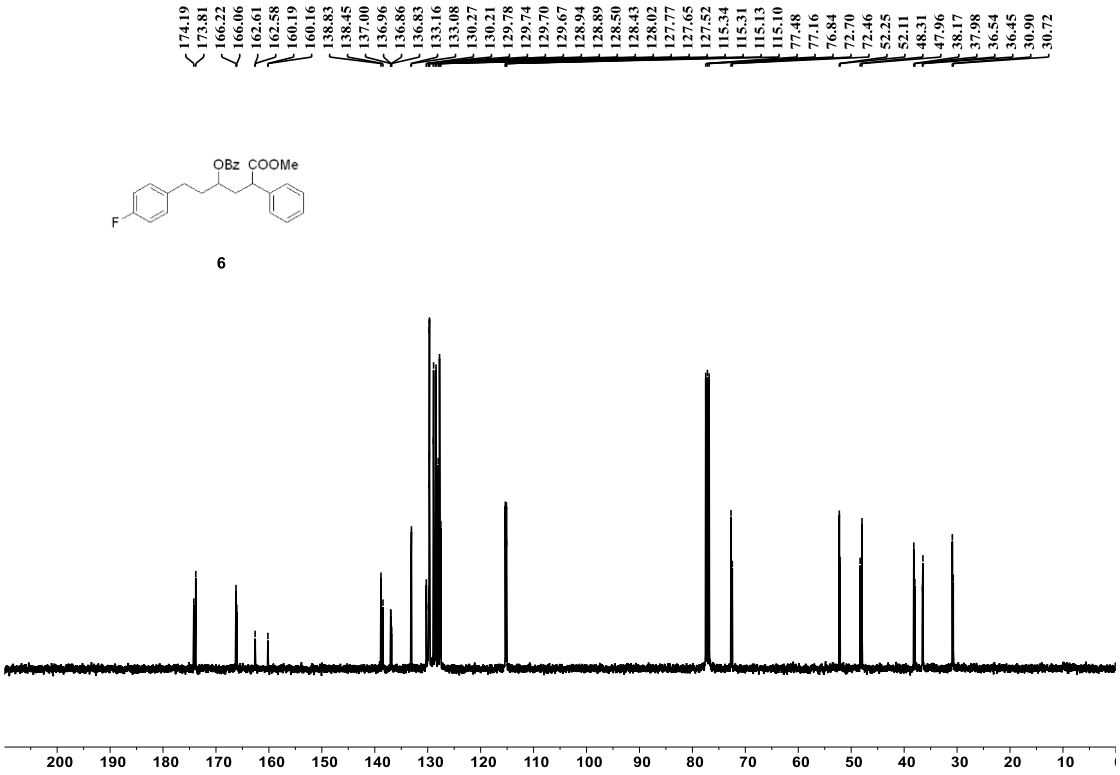
^{13}C NMR (101 MHz, $CDCl_3$)



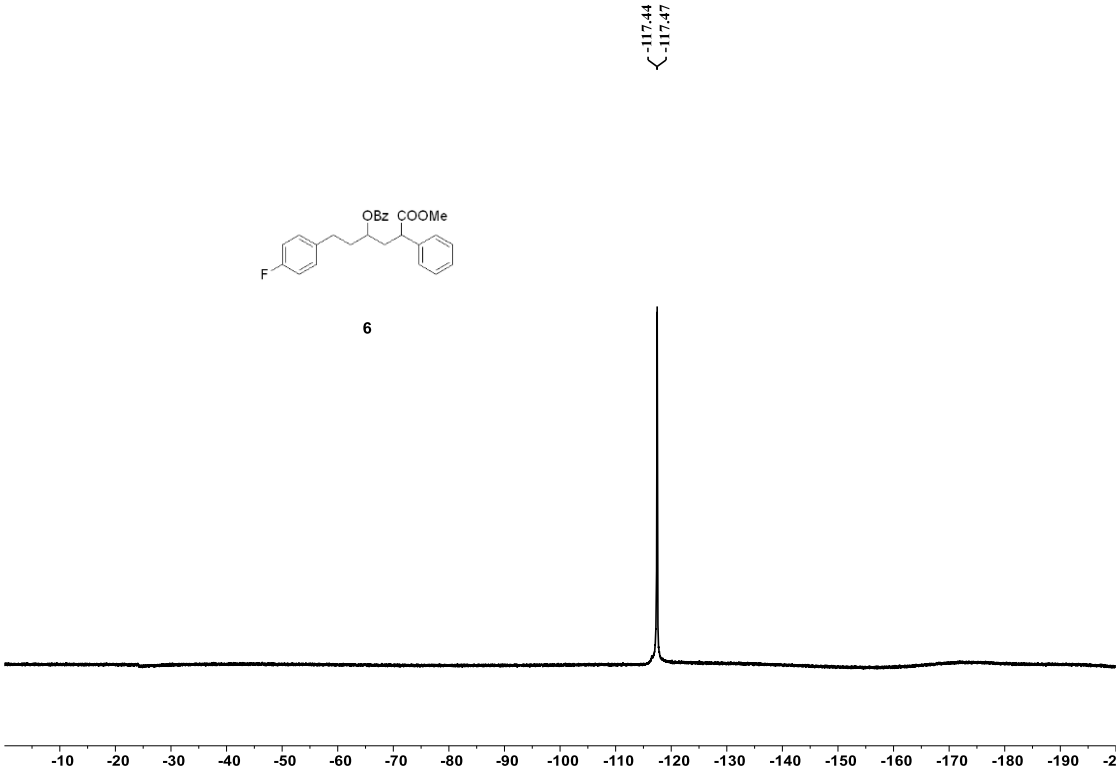
^{1}H NMR (500 MHz, $CDCl_3$)



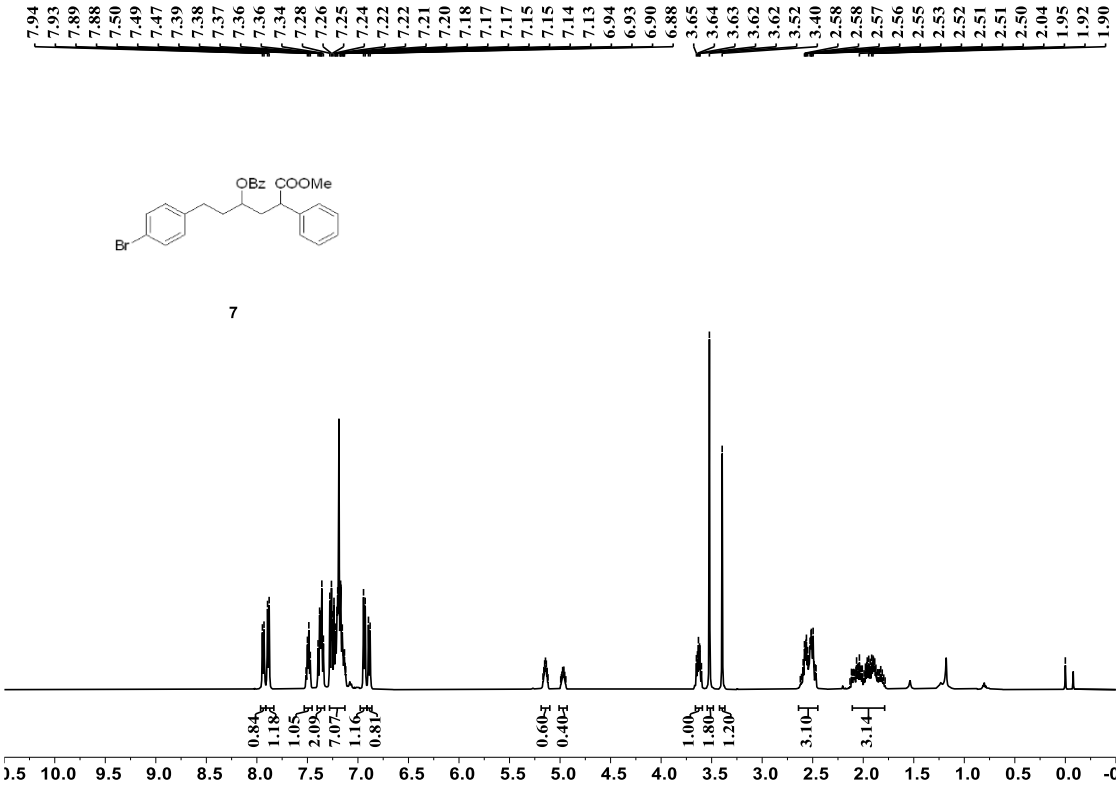
^{13}C NMR (101 MHz, $CDCl_3$)



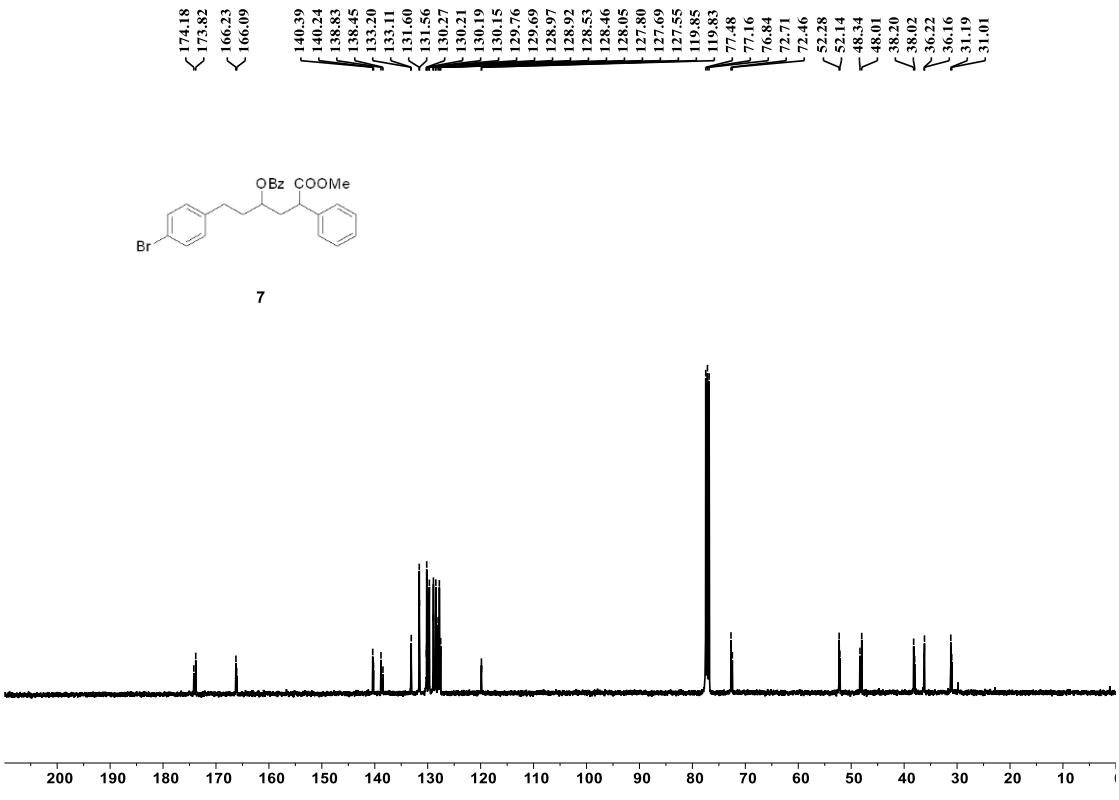
^{19}F NMR (377 MHz, $CDCl_3$)



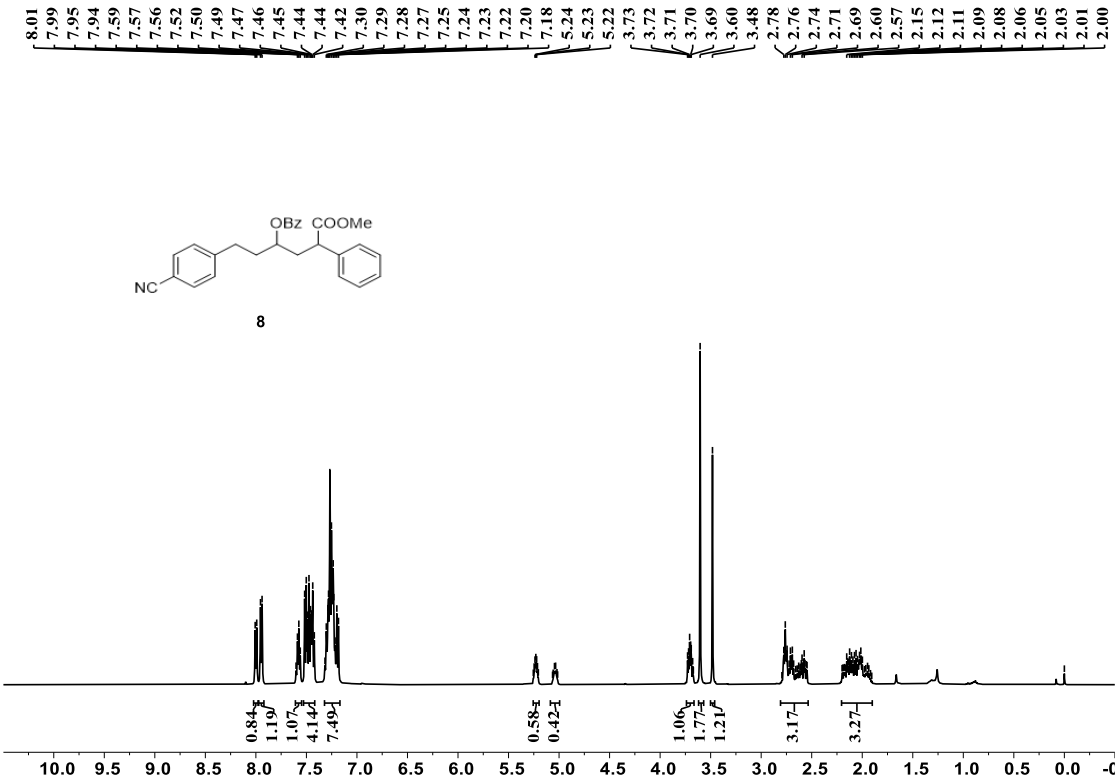
^{1}H NMR (400 MHz, $CDCl_3$)



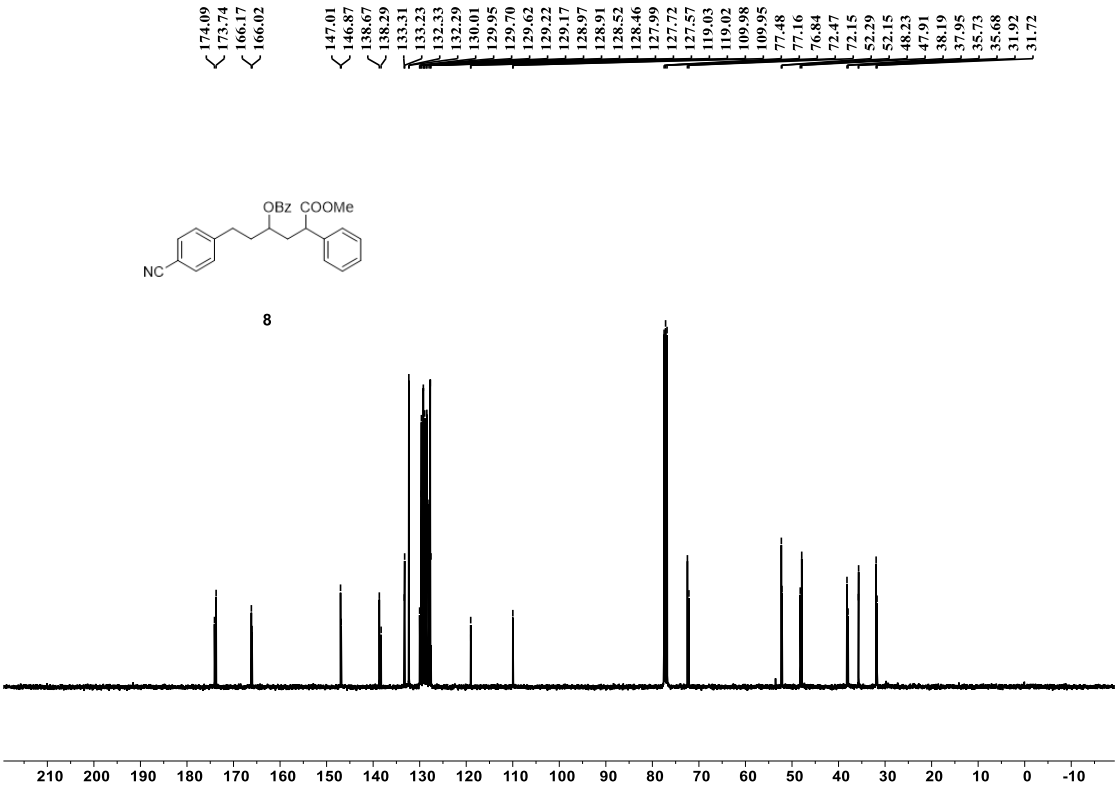
^{13}C NMR (101 MHz, $CDCl_3$)



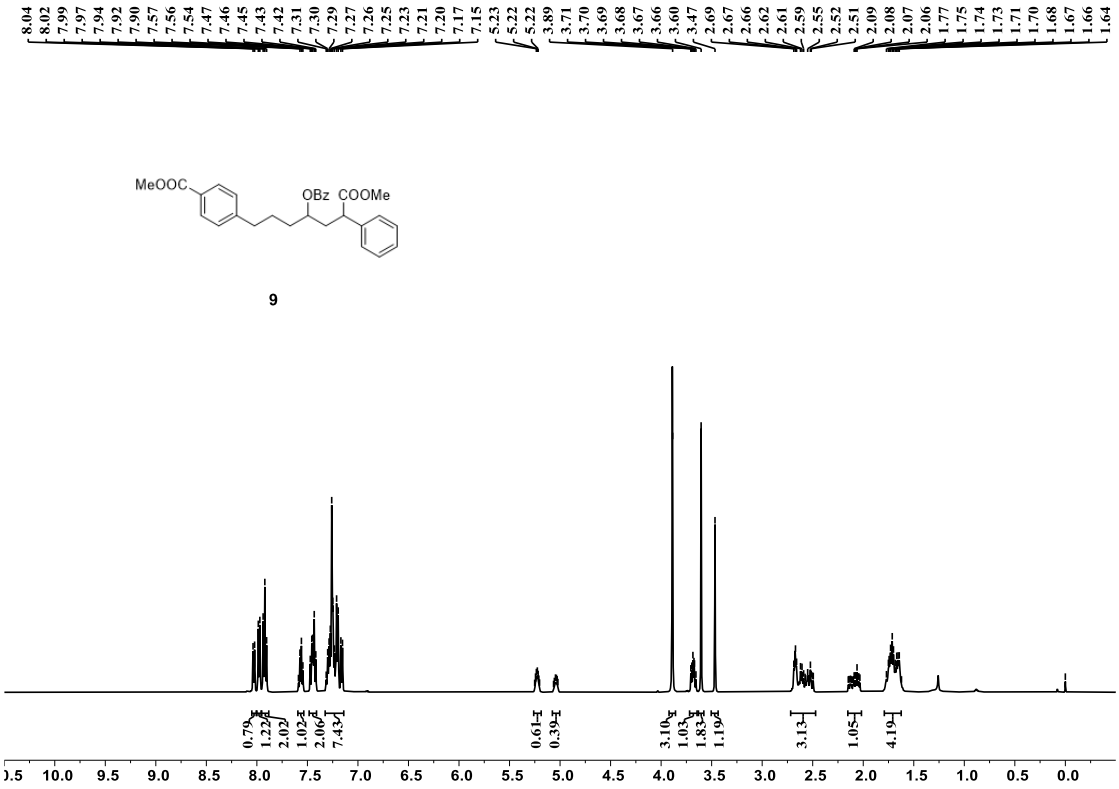
^{1}H NMR (500 MHz, $CDCl_3$)



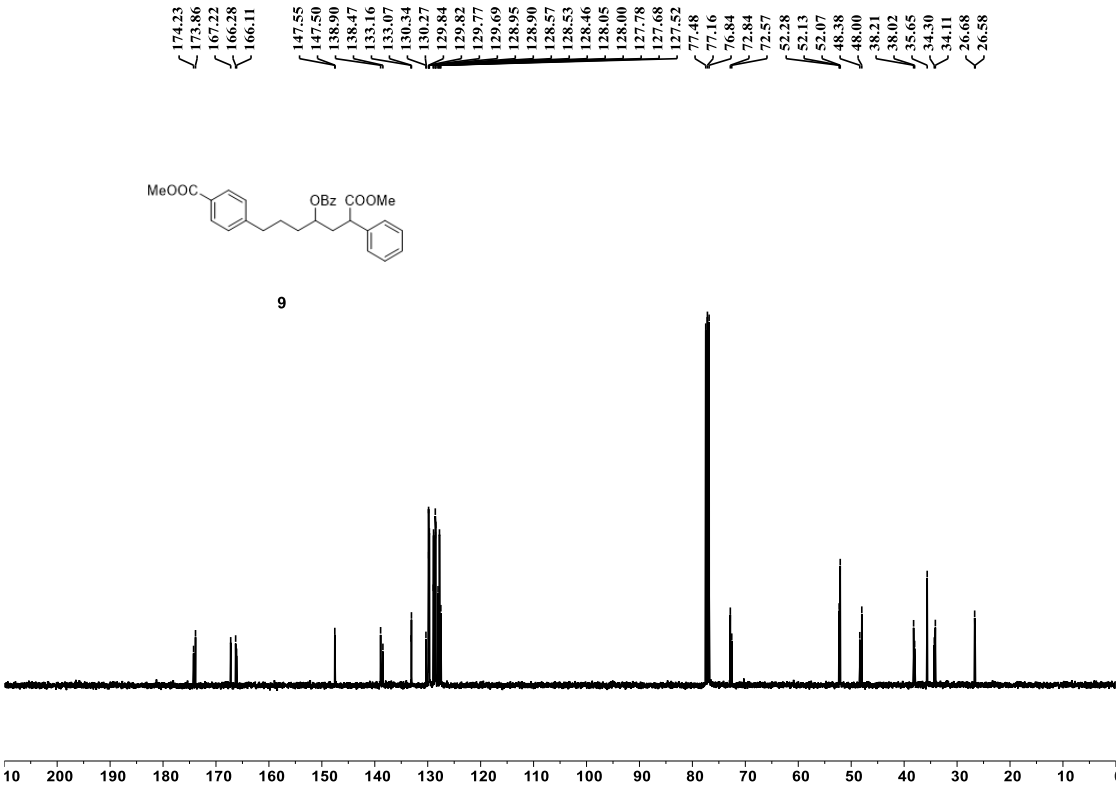
^{13}C NMR (101 MHz, $CDCl_3$)



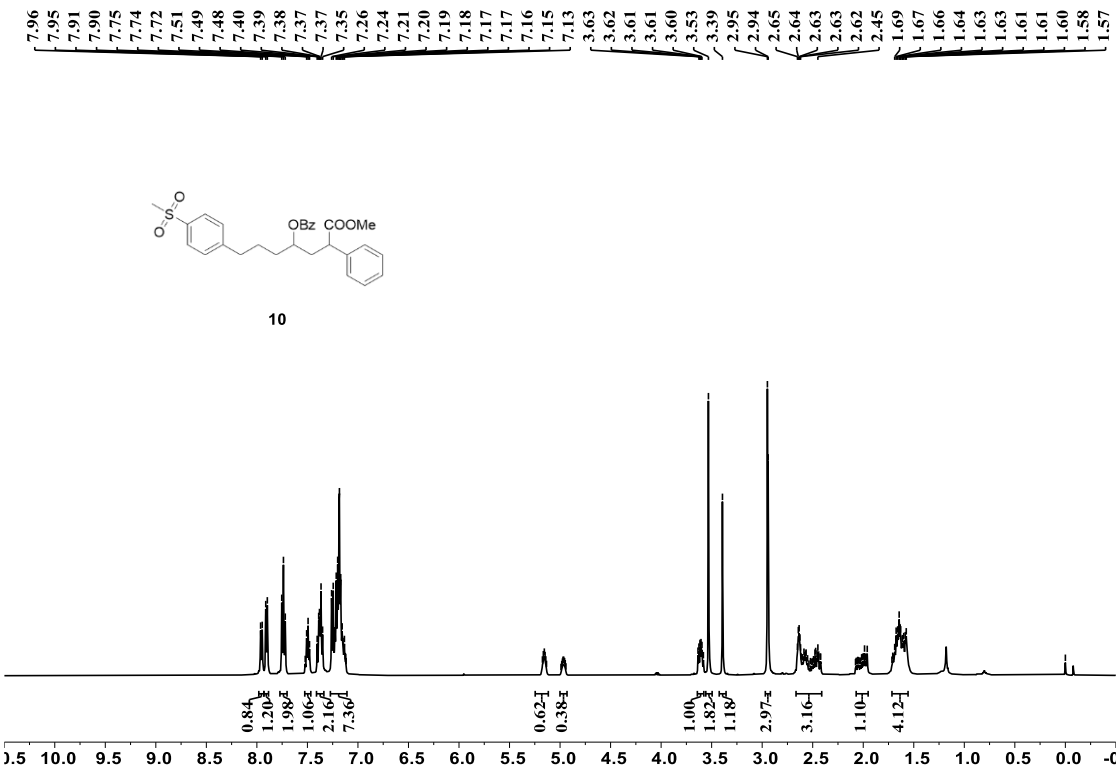
^{1}H NMR (500 MHz, $CDCl_3$)



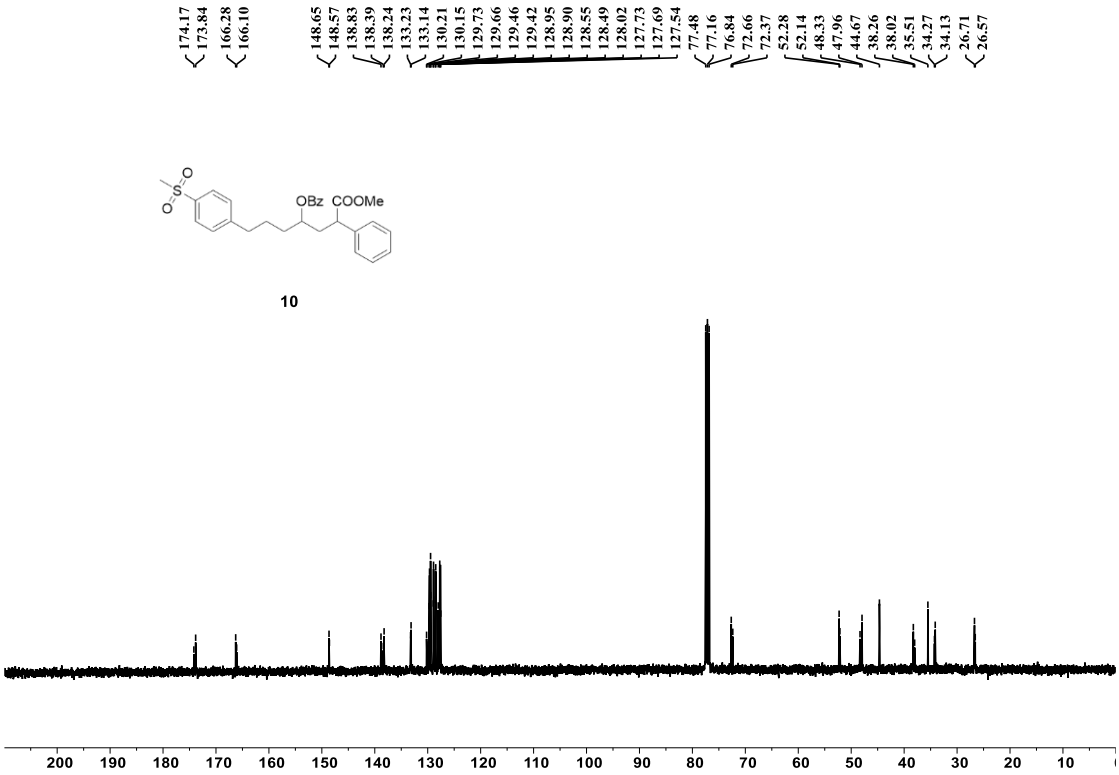
^{13}C NMR (101 MHz, $CDCl_3$)



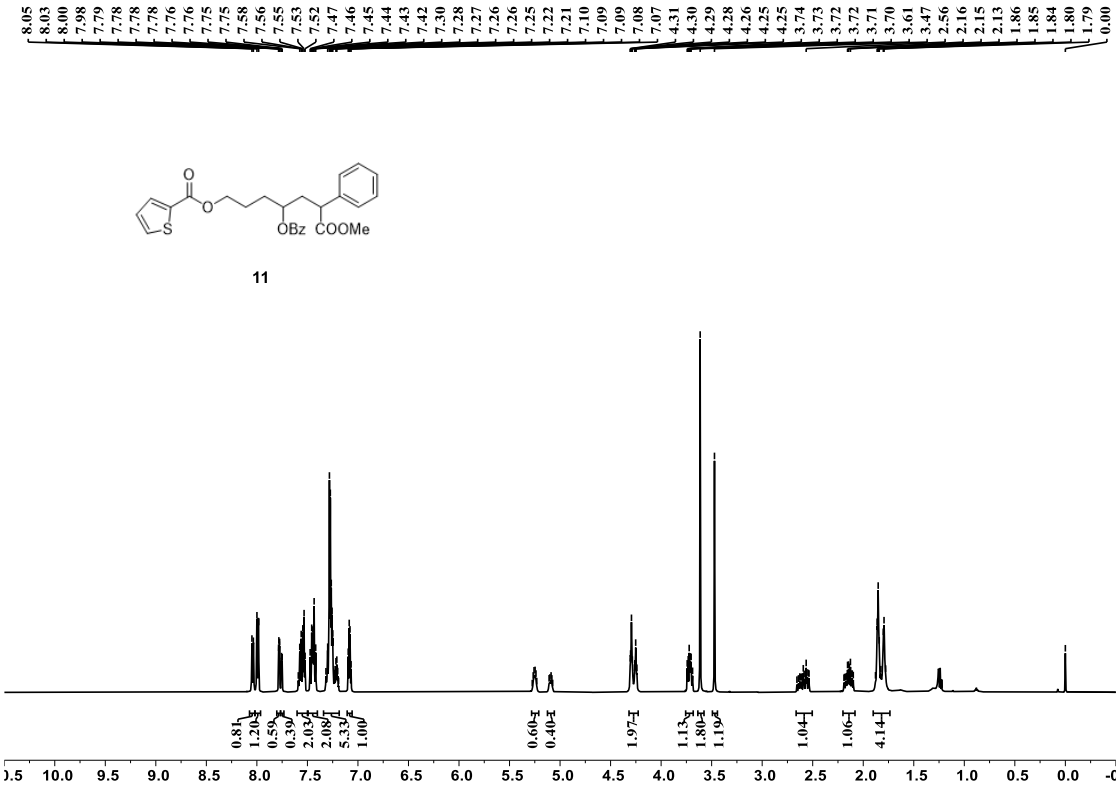
^{1}H NMR (500 MHz, $CDCl_3$)



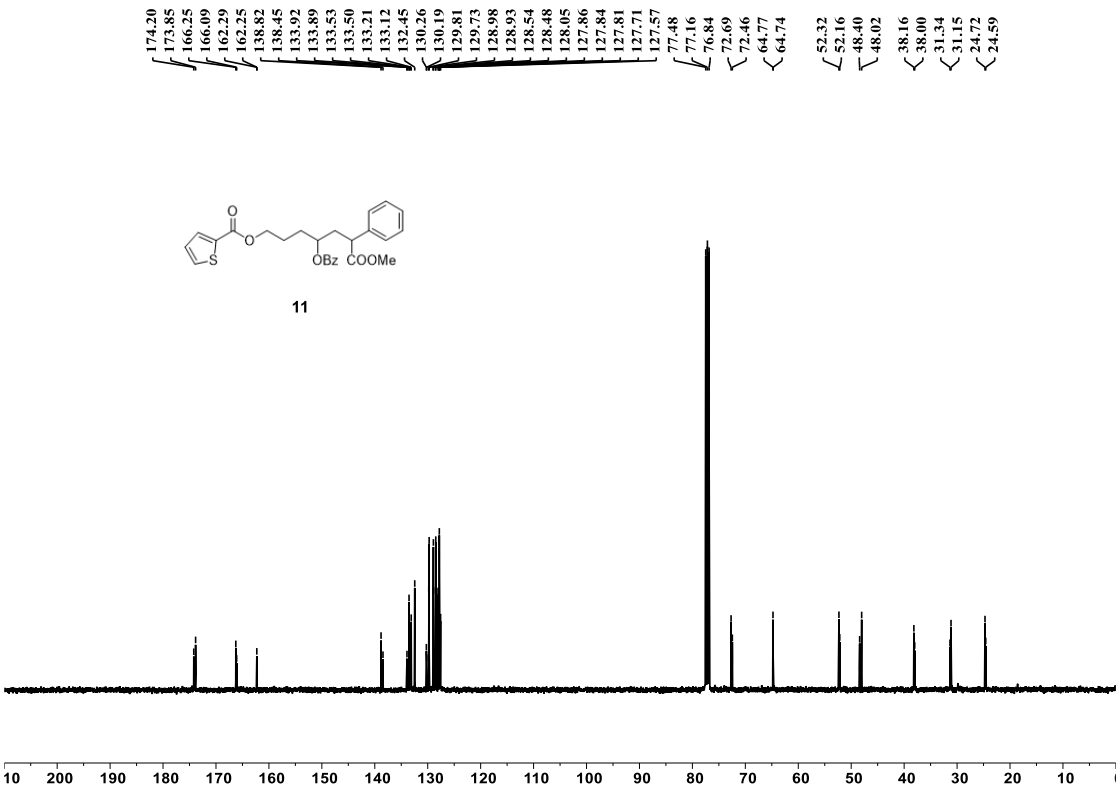
^{13}C NMR (101 MHz, $CDCl_3$)



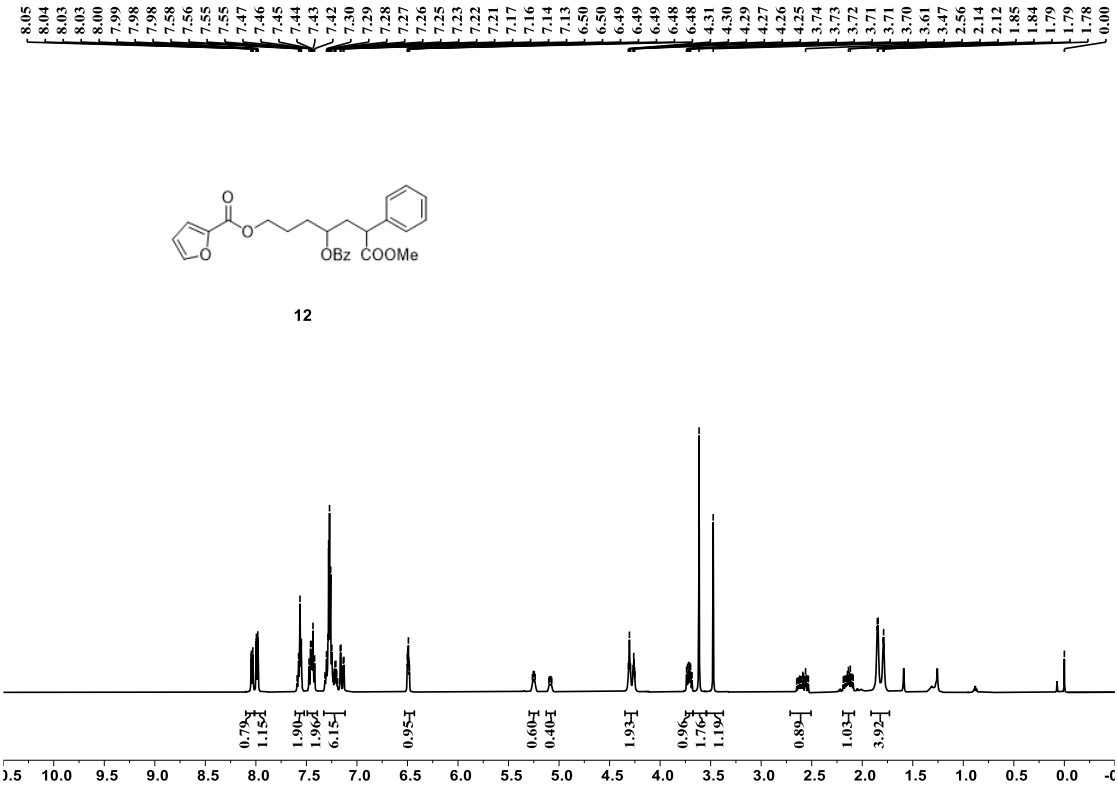
^{1}H NMR (500 MHz, $CDCl_3$)



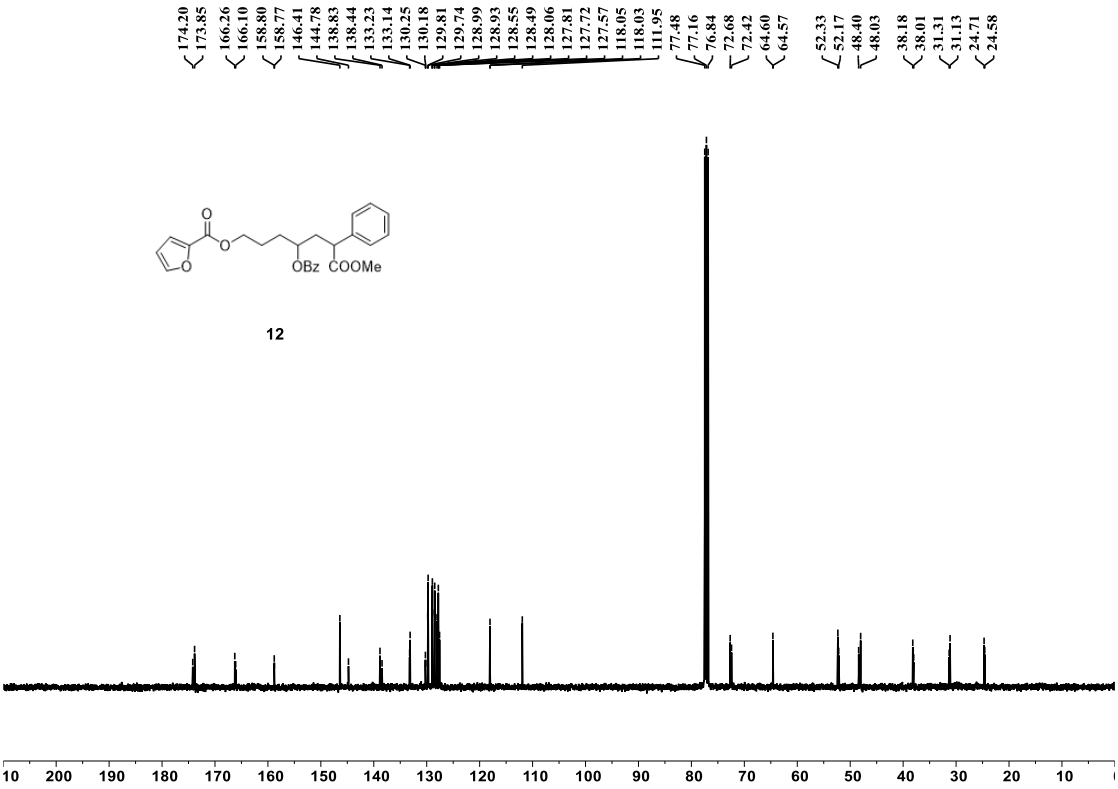
^{13}C NMR (101 MHz, $CDCl_3$)



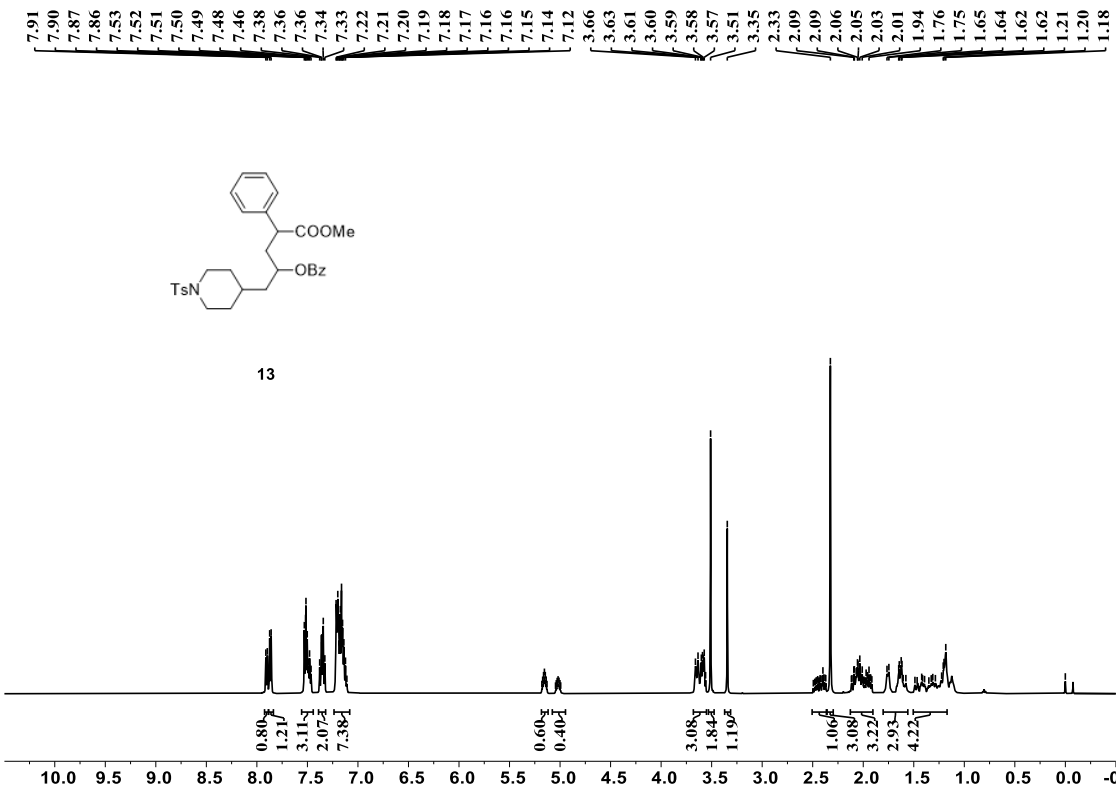
^{1}H NMR (500 MHz, $CDCl_3$)



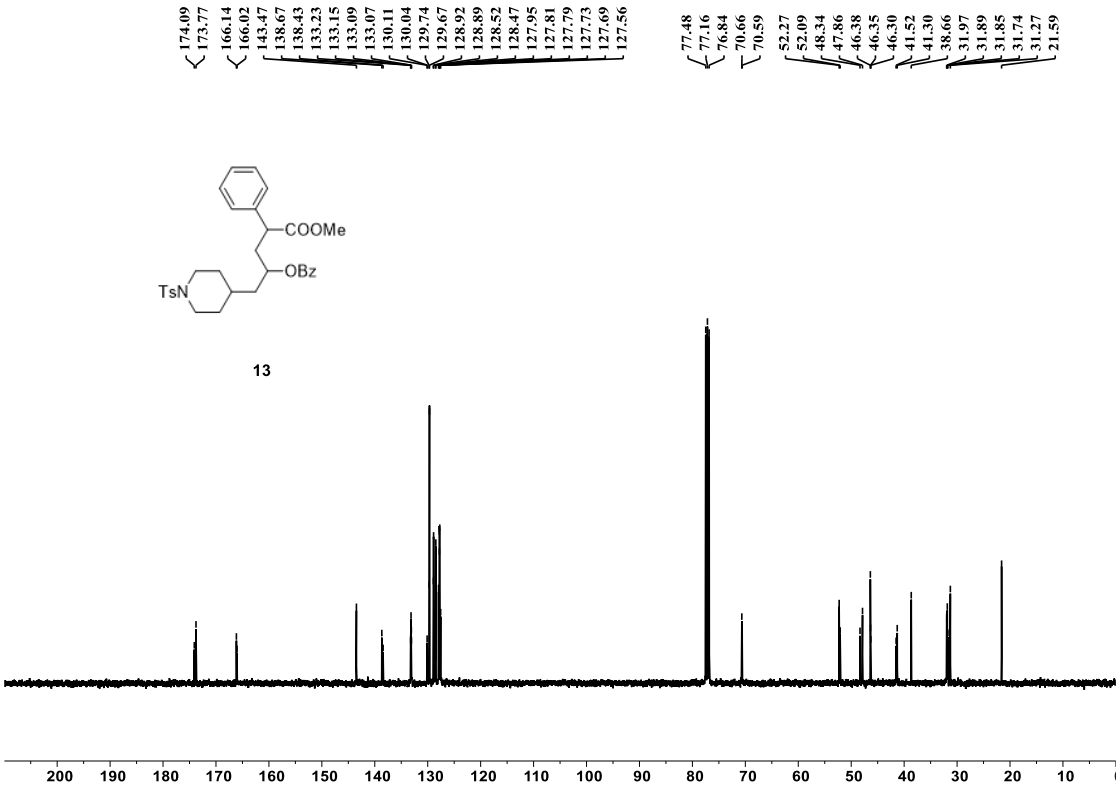
^{13}C NMR (101 MHz, $CDCl_3$)



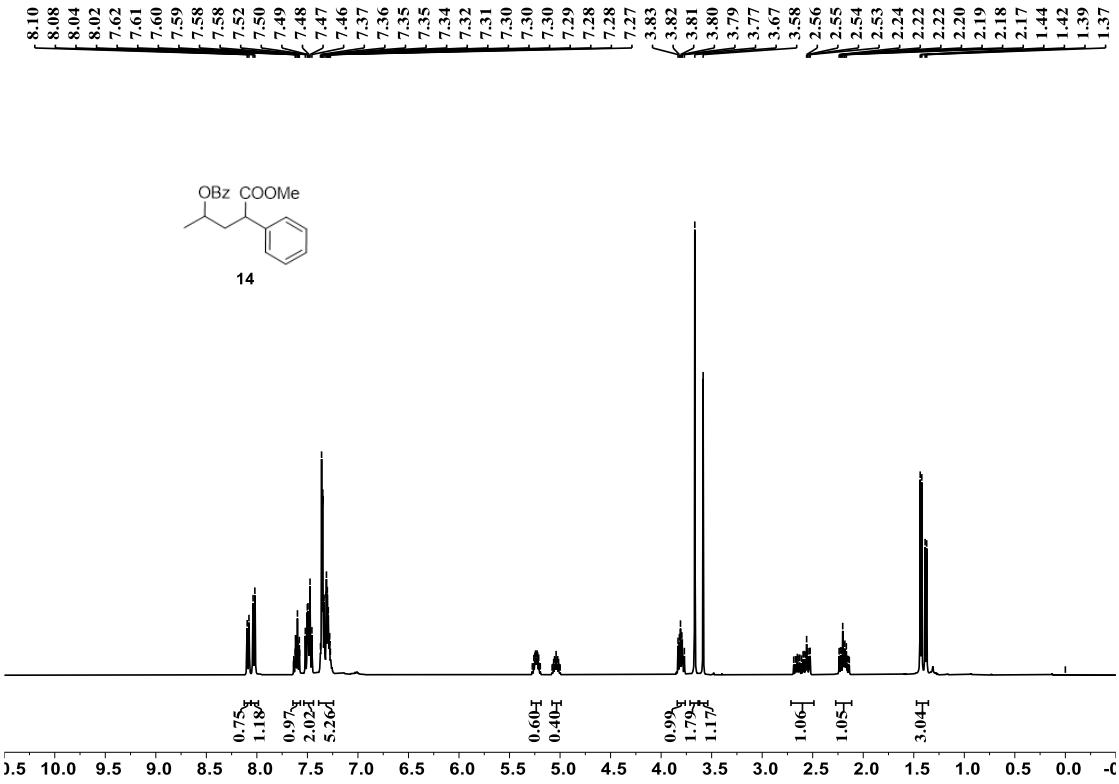
^{1}H NMR (500 MHz, $CDCl_3$)



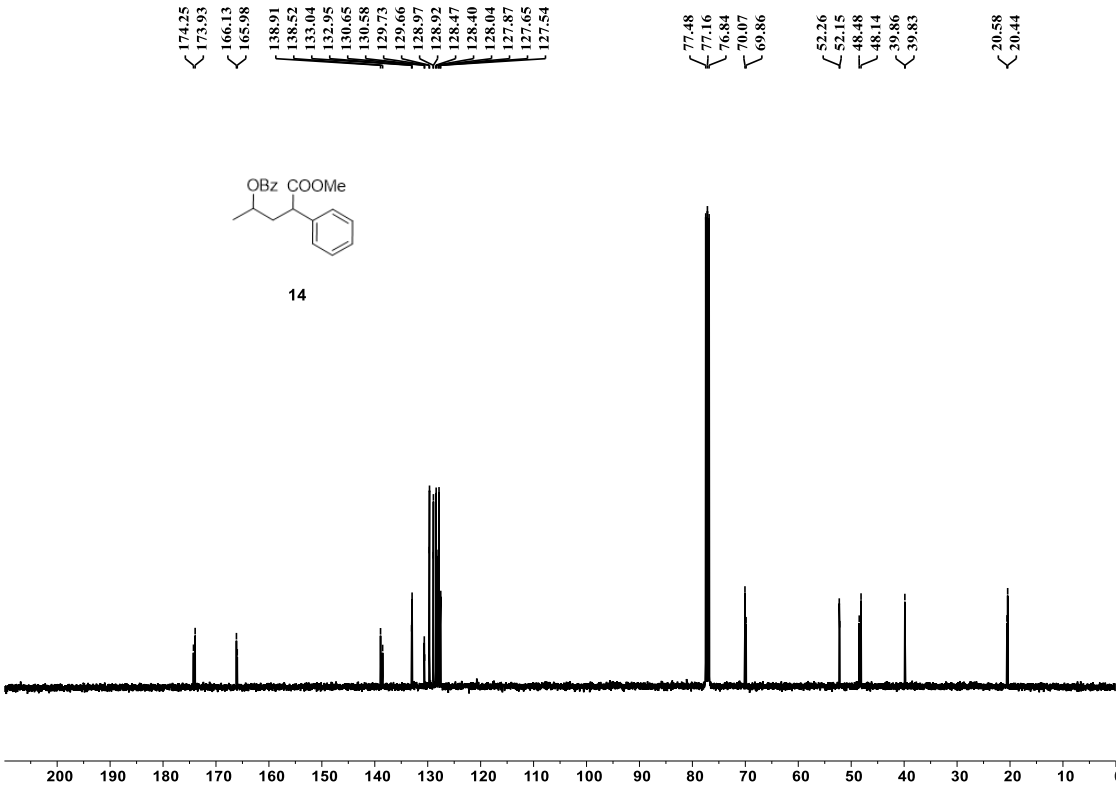
^{13}C NMR (101 MHz, $CDCl_3$)



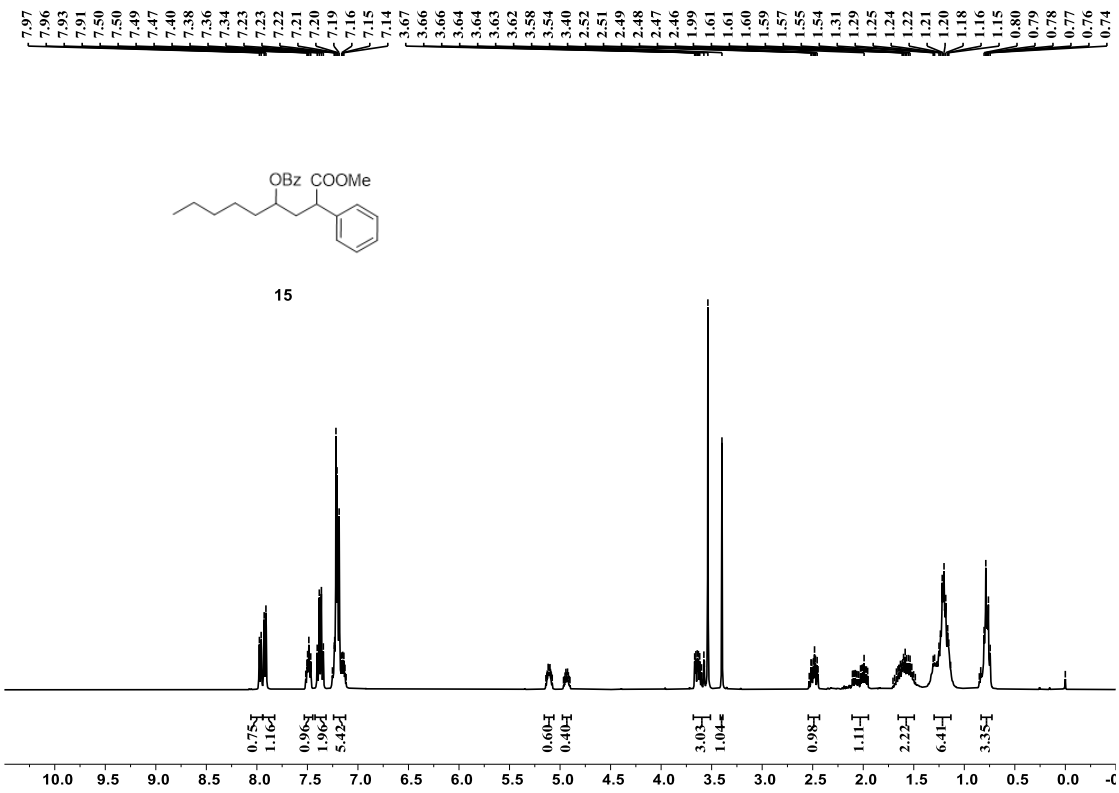
^{1}H NMR (400 MHz, $CDCl_3$)



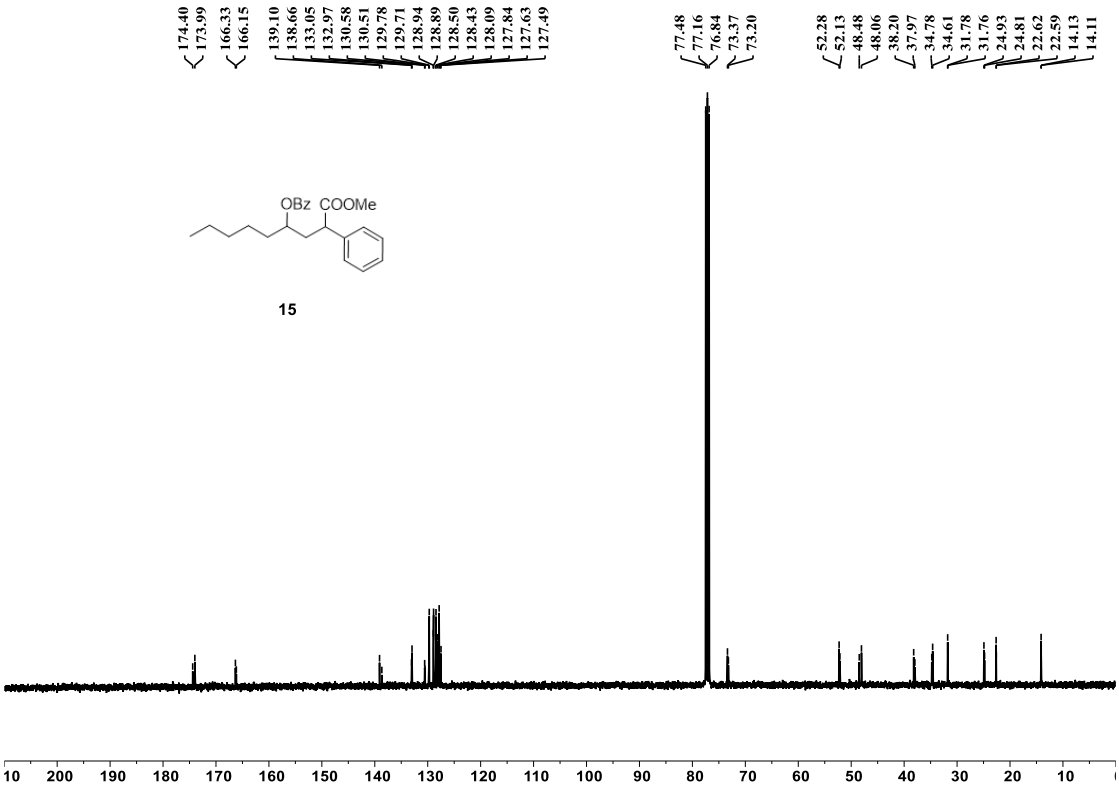
^{13}C NMR (101 MHz, $CDCl_3$)



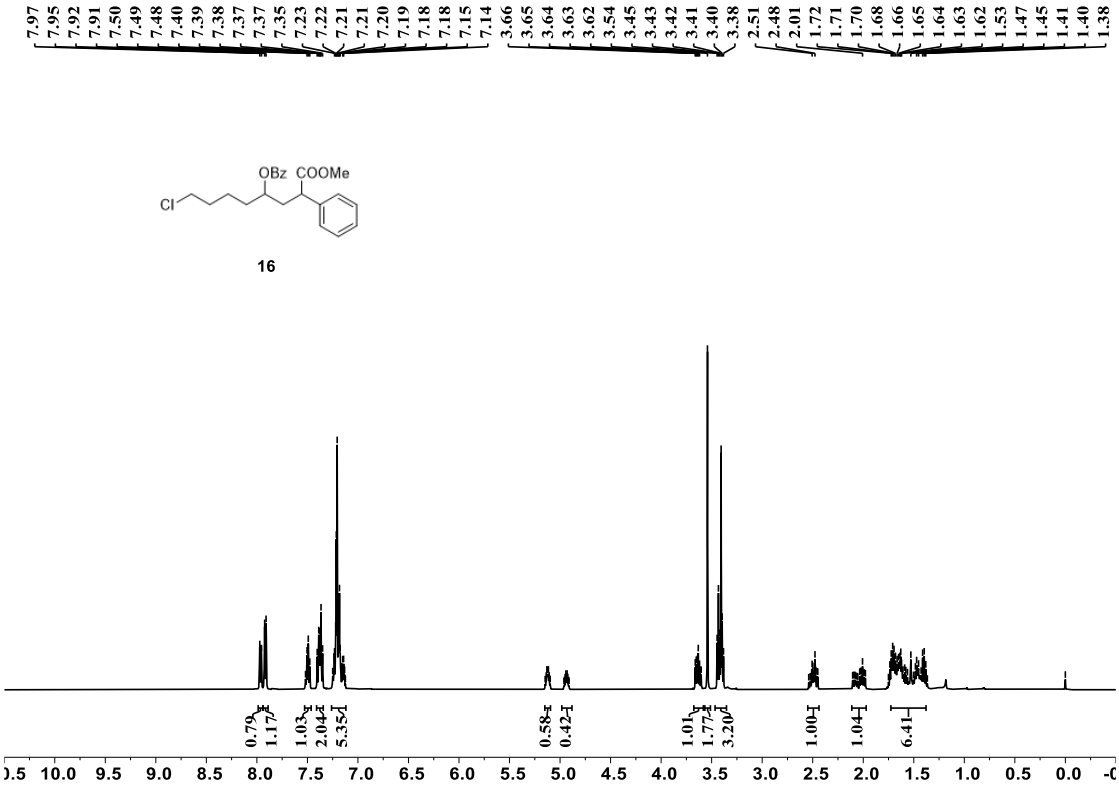
^{1}H NMR (400 MHz, $CDCl_3$)



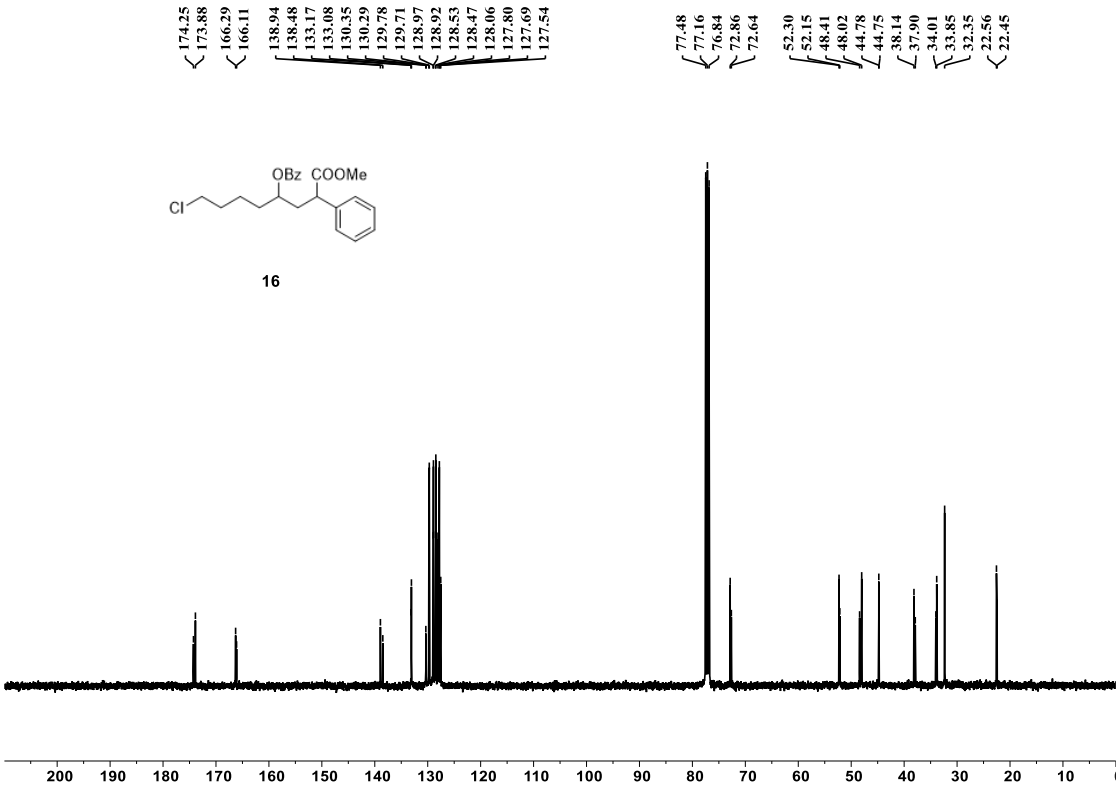
^{13}C NMR (101 MHz, $CDCl_3$)



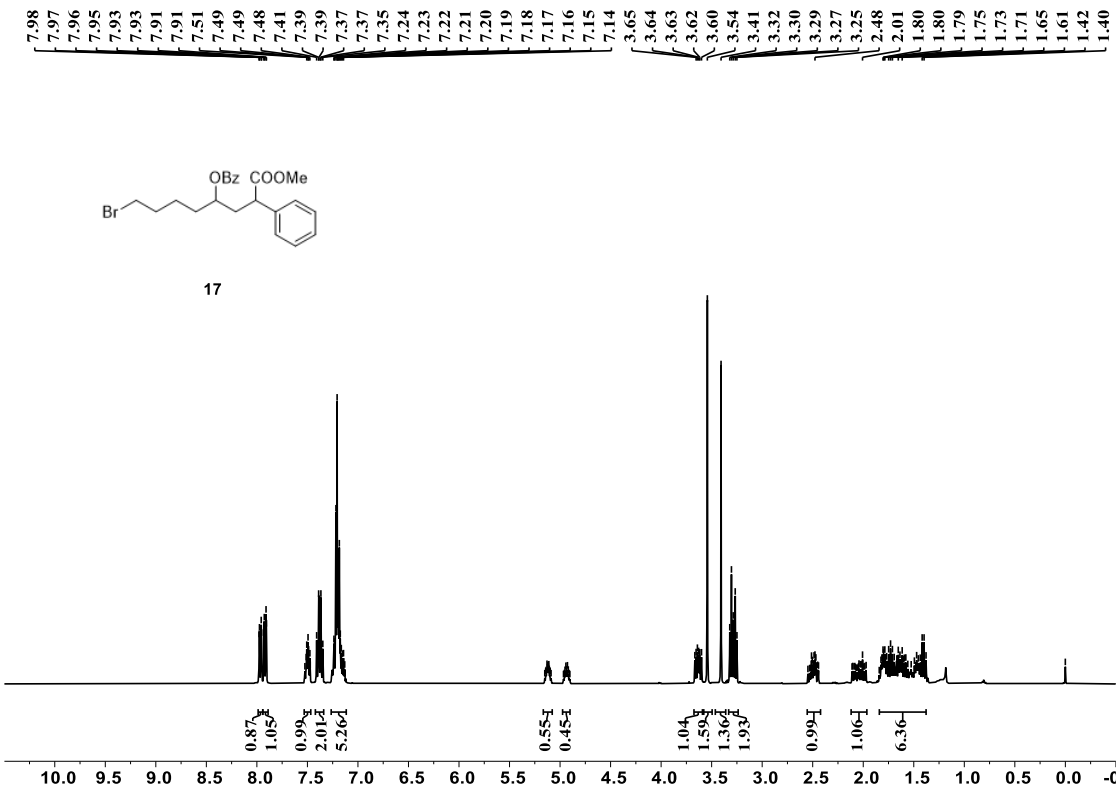
^{1}H NMR (500 MHz, $CDCl_3$)



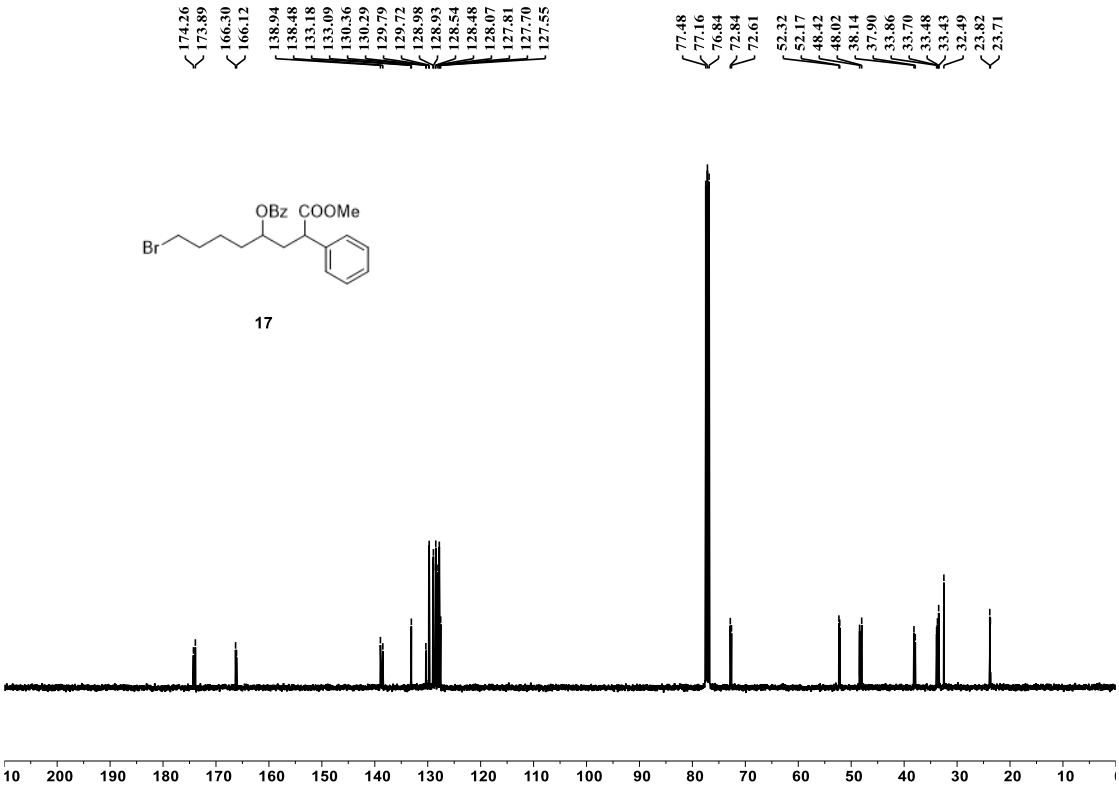
^{13}C NMR (101 MHz, $CDCl_3$)



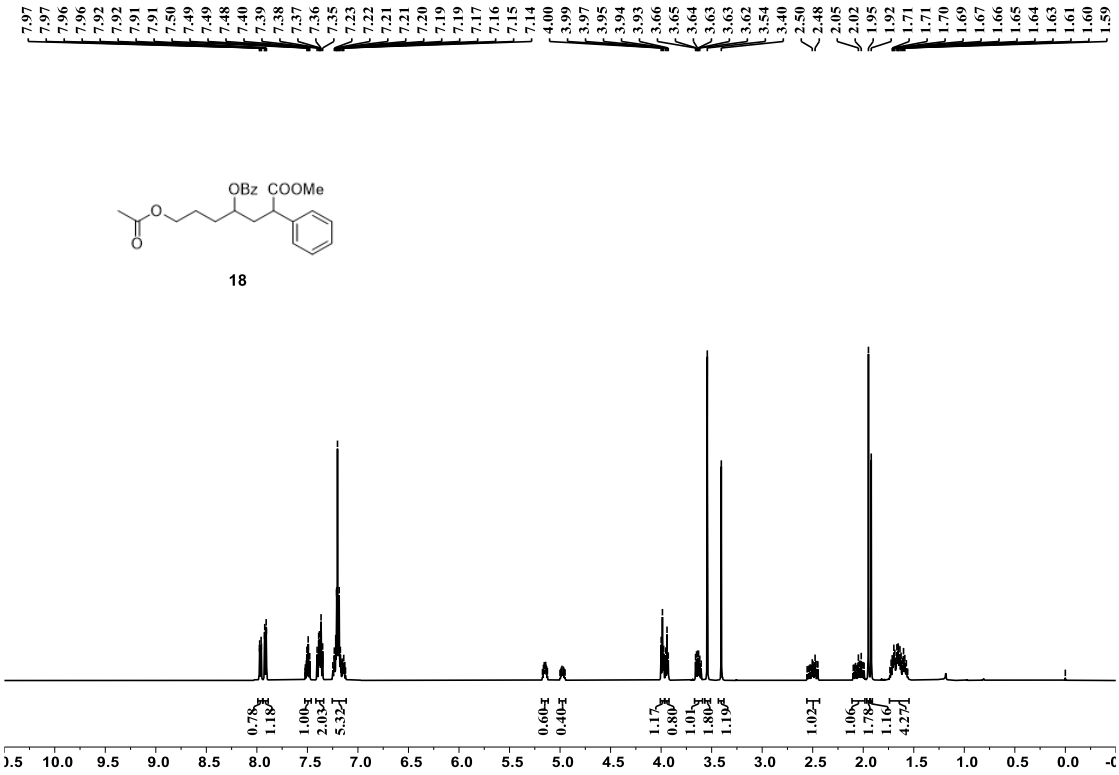
^{1}H NMR (400 MHz, $CDCl_3$)



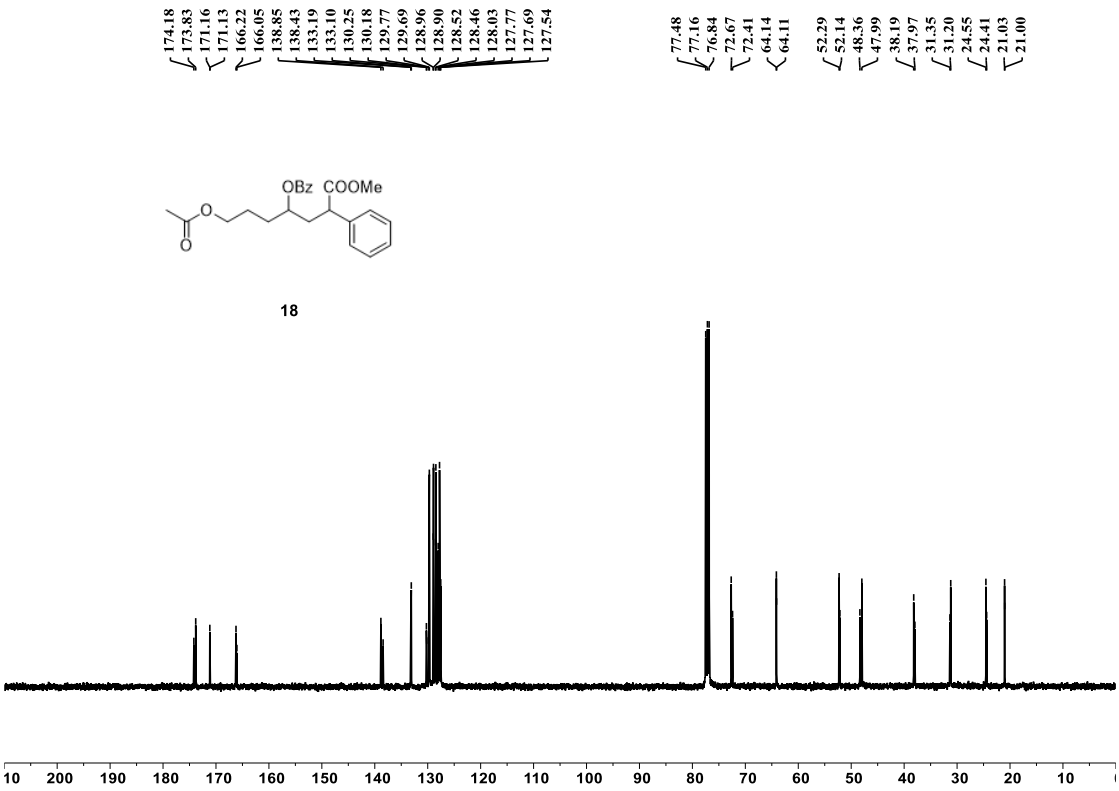
^{13}C NMR (101 MHz, $CDCl_3$)



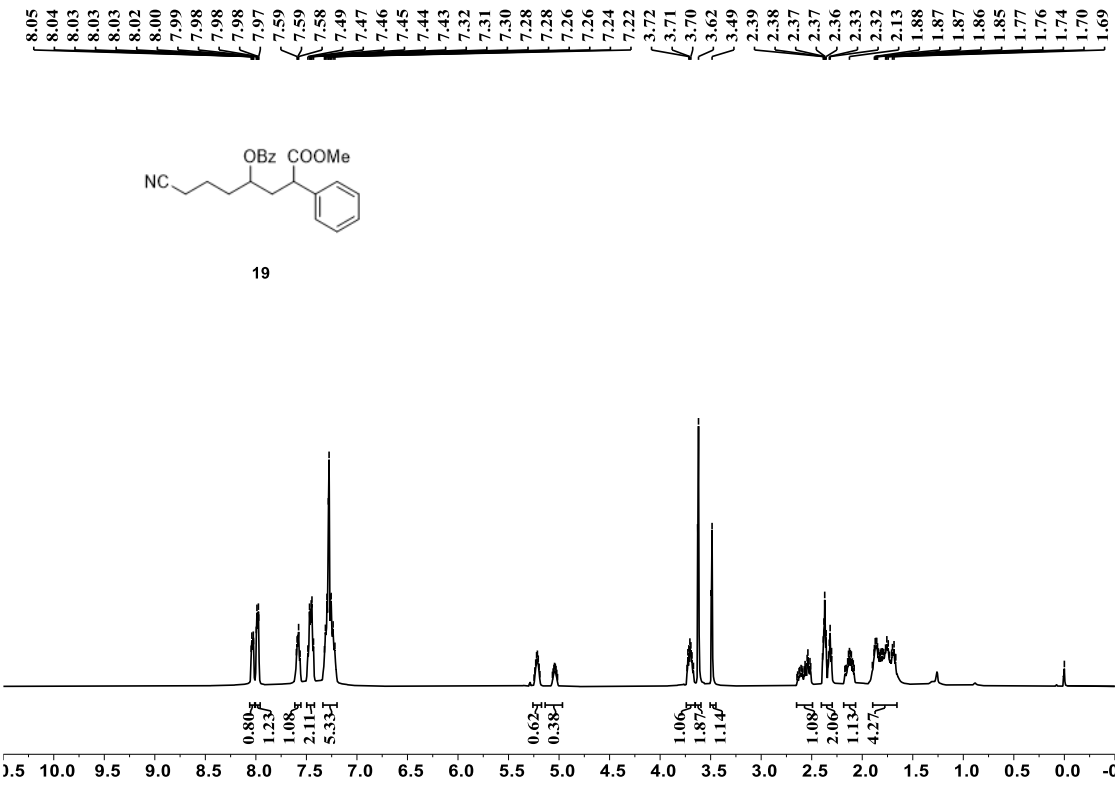
^{1}H NMR (500 MHz, $CDCl_3$)



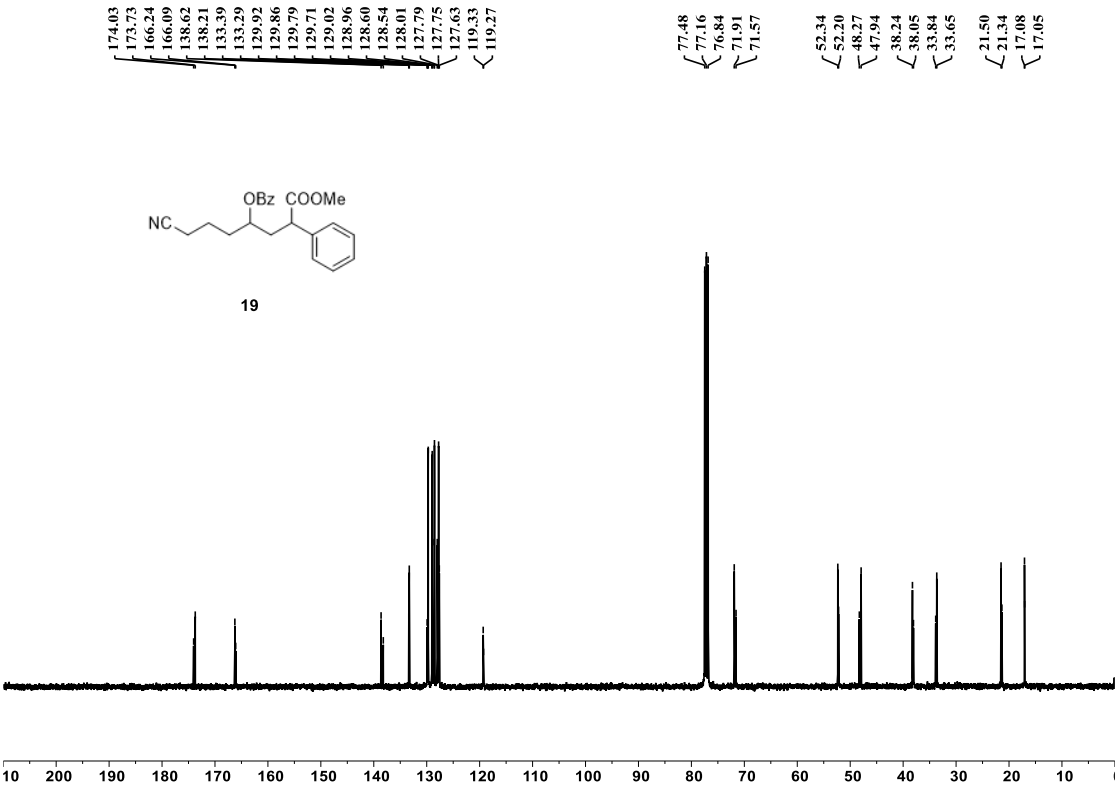
^{13}C NMR (101 MHz, $CDCl_3$)



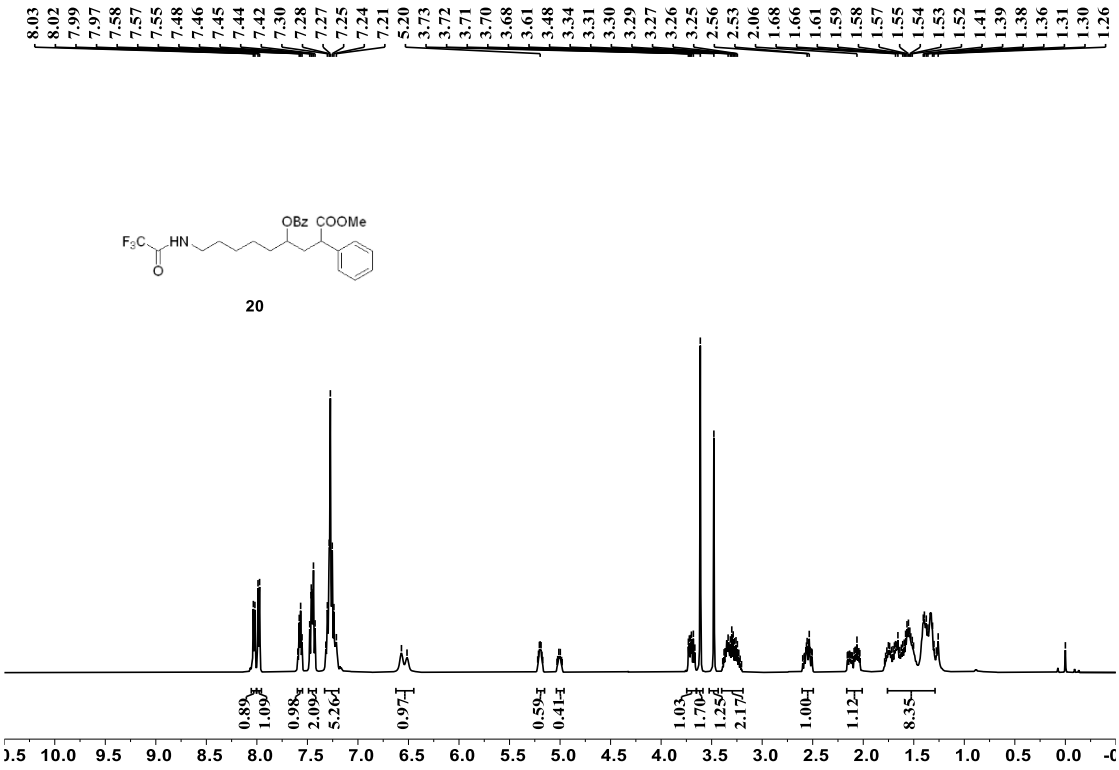
^{1}H NMR (500 MHz, $CDCl_3$)



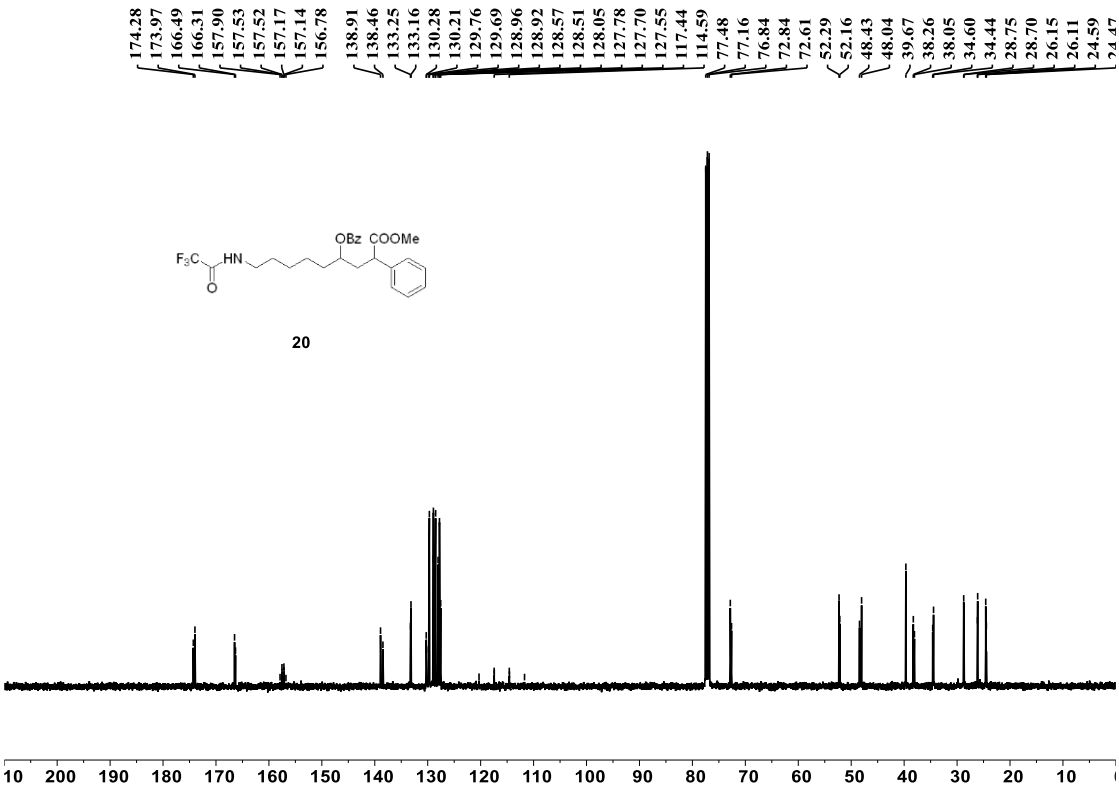
^{13}C NMR (101 MHz, $CDCl_3$)



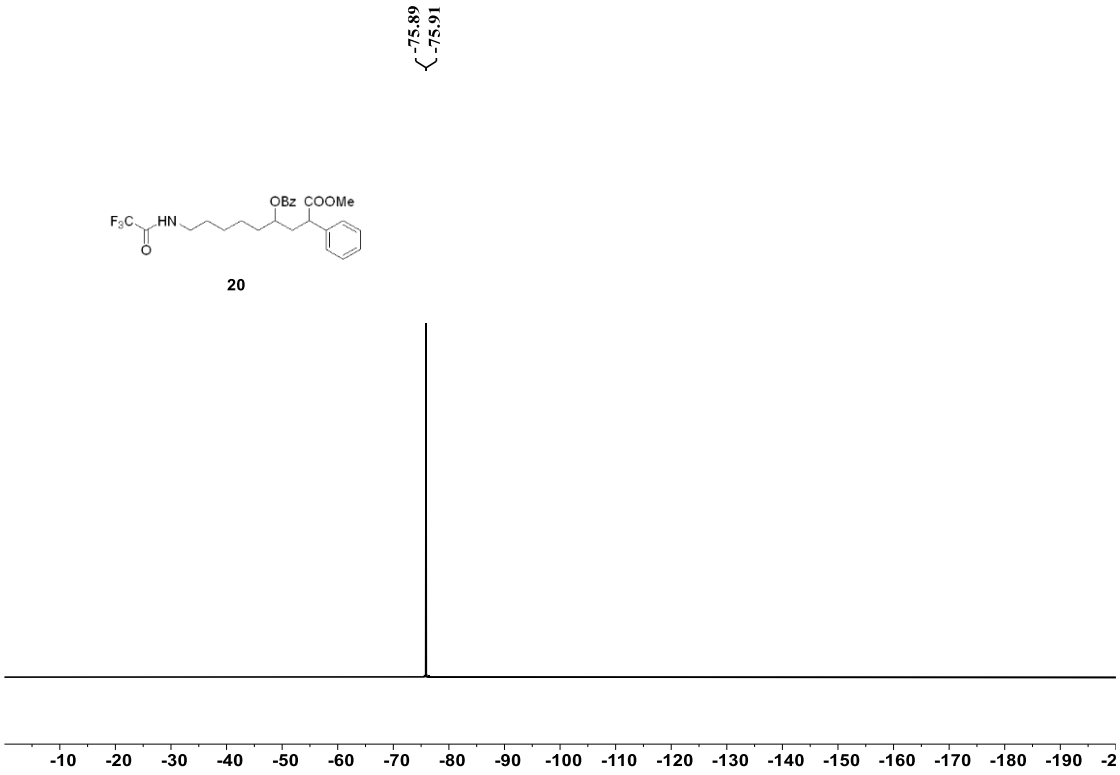
^{1}H NMR (500 MHz, $CDCl_3$)



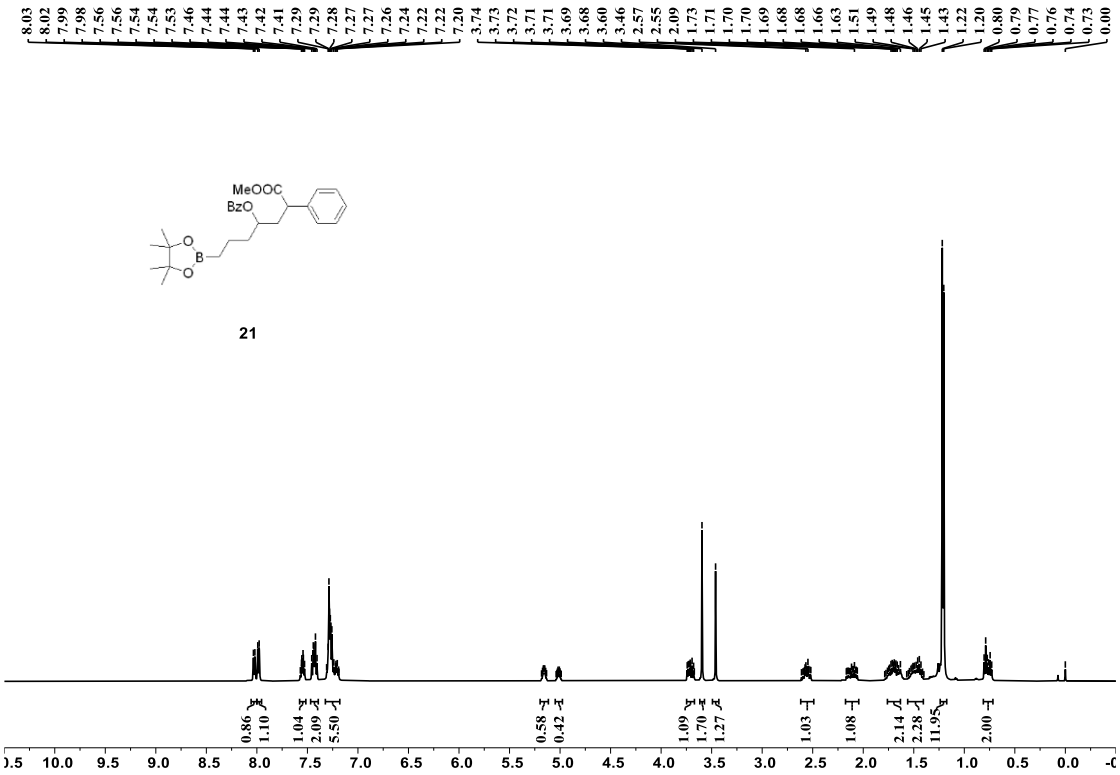
^{13}C NMR (101 MHz, $CDCl_3$)



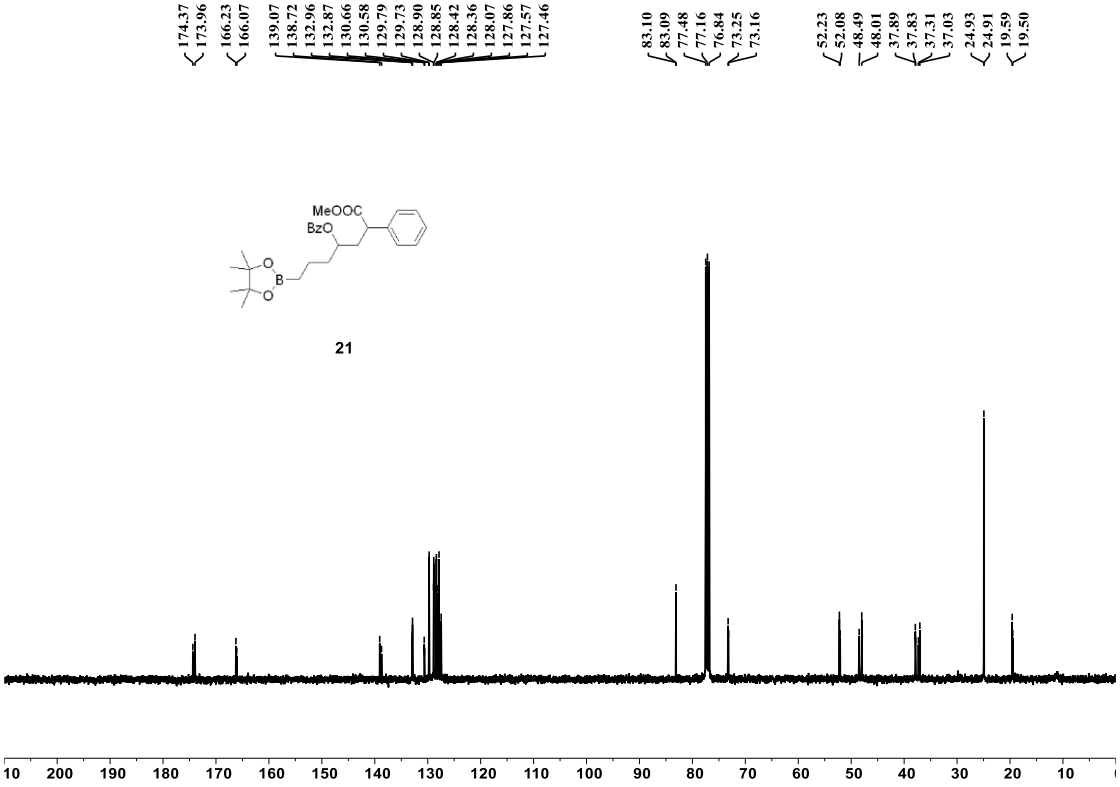
^{19}F NMR (377 MHz, $CDCl_3$)



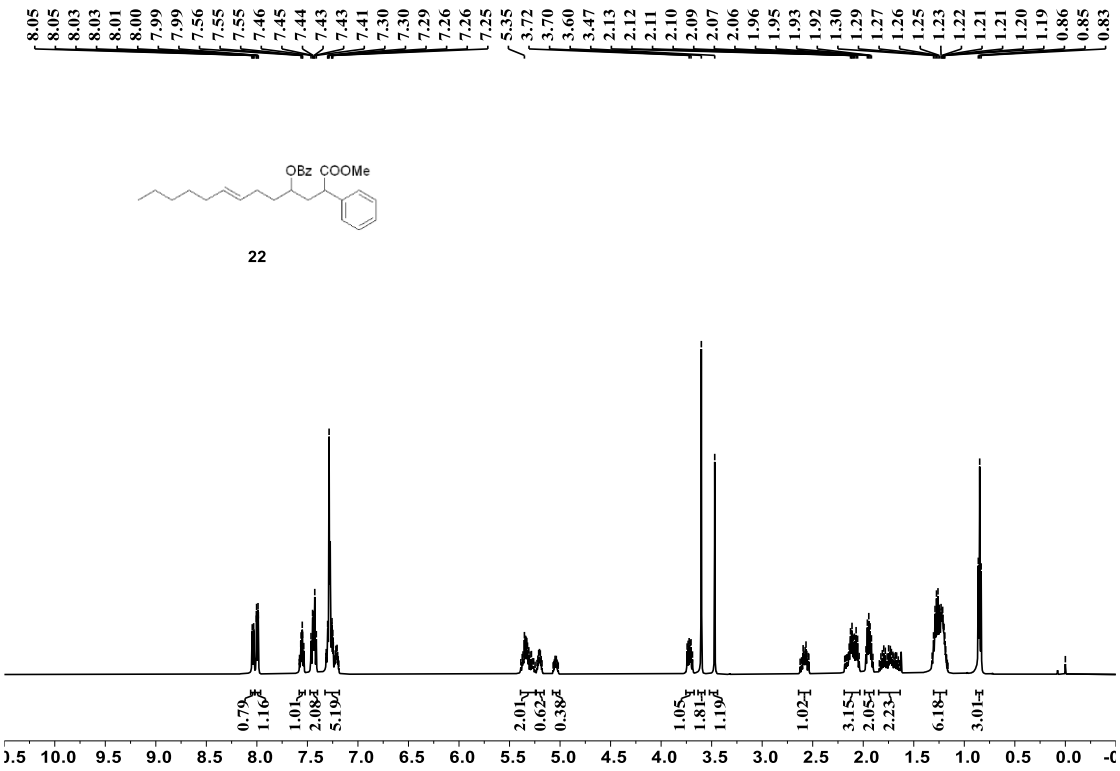
^{1}H NMR (500 MHz, $CDCl_3$)



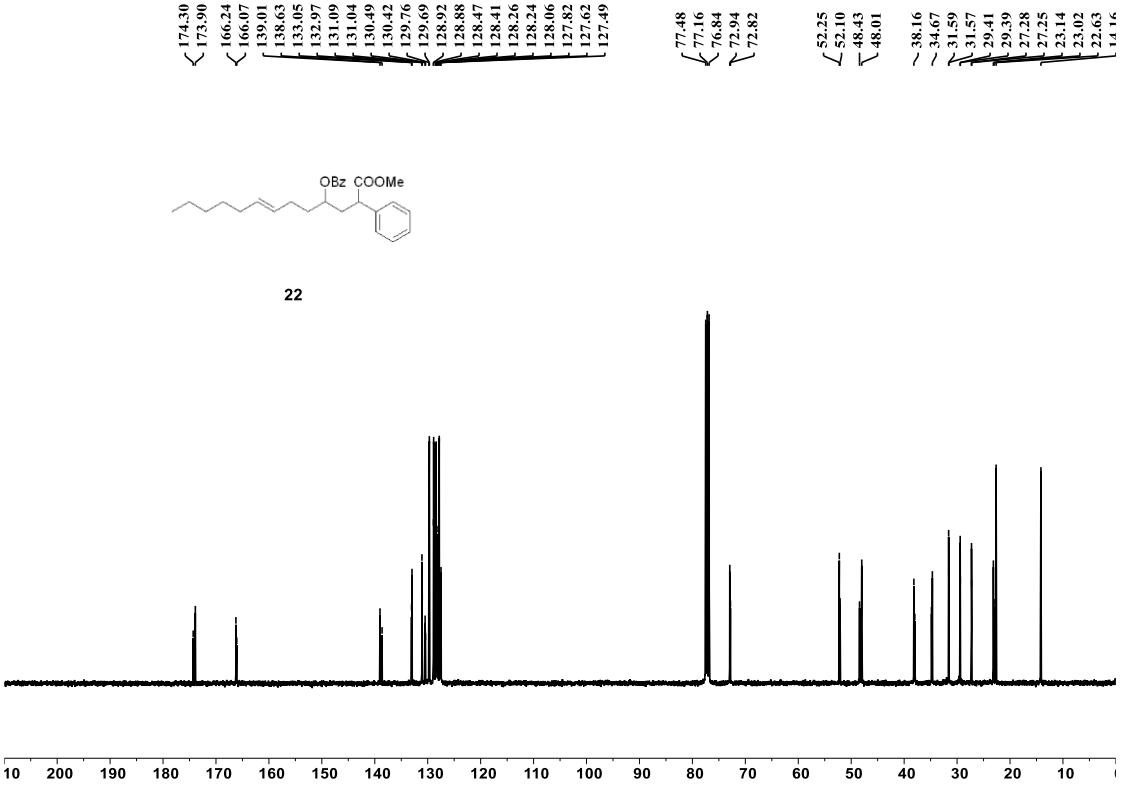
^{13}C NMR (101 MHz, $CDCl_3$)



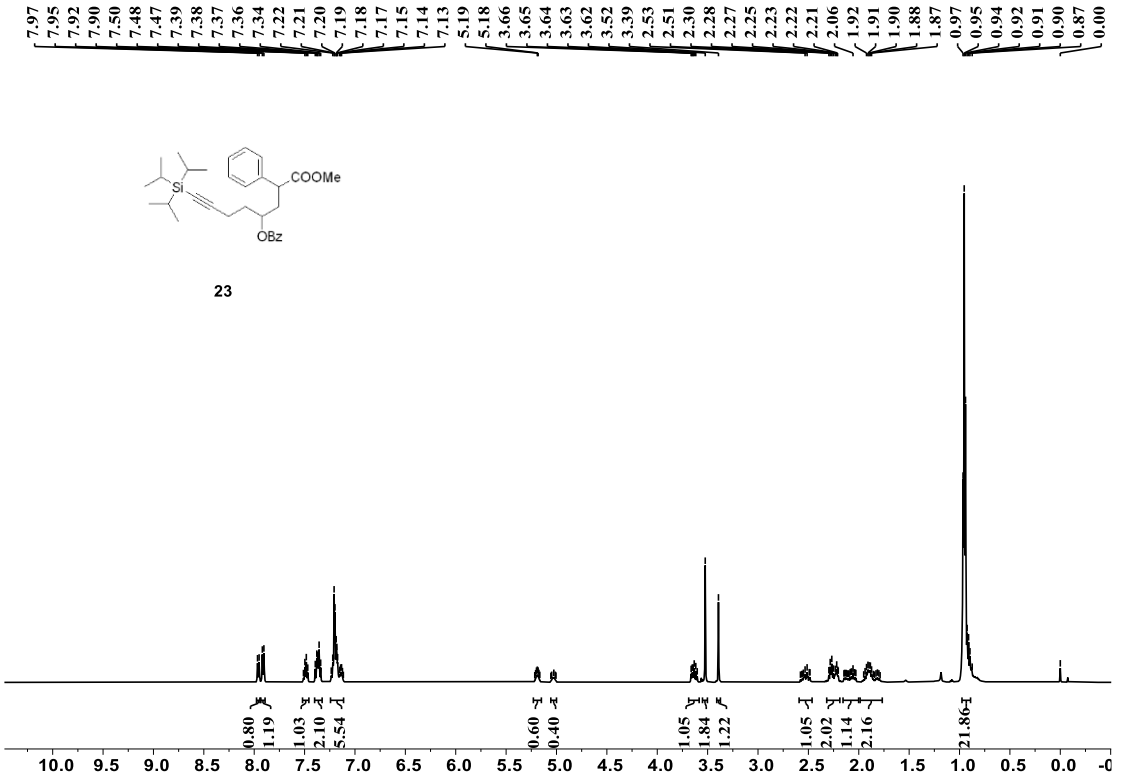
^{1}H NMR (500 MHz, $CDCl_3$)



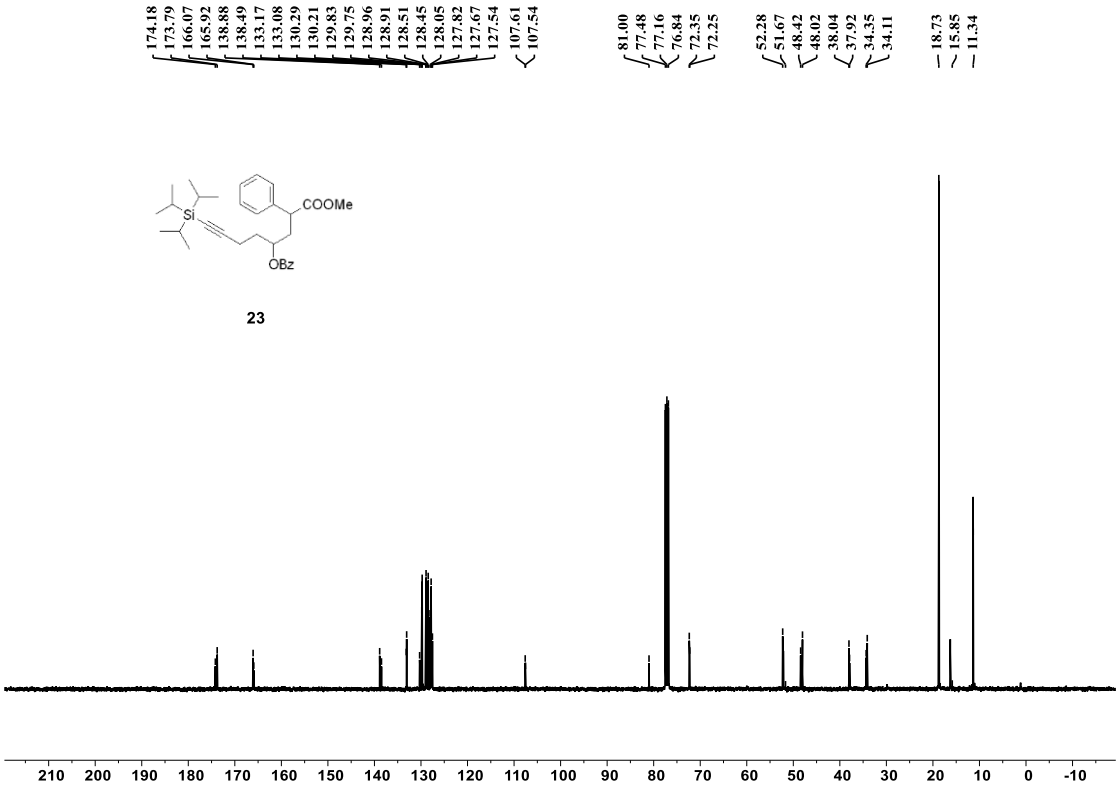
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

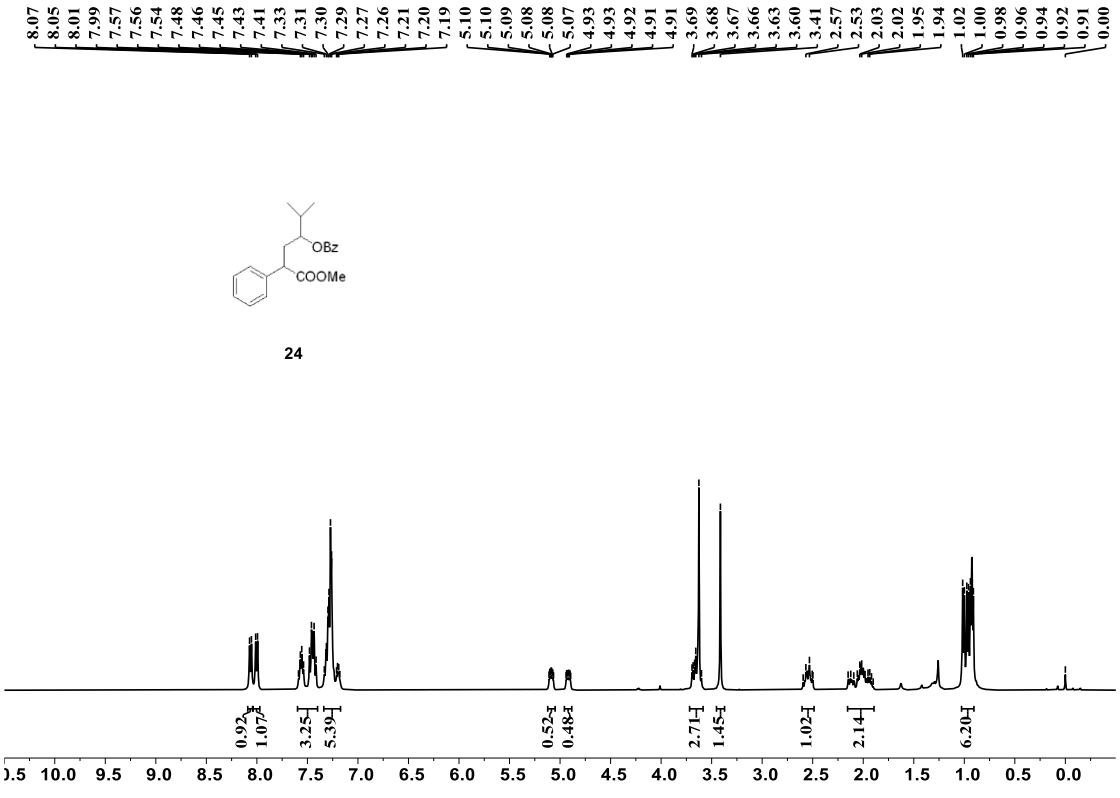


^{13}C NMR (101 MHz, $CDCl_3$)



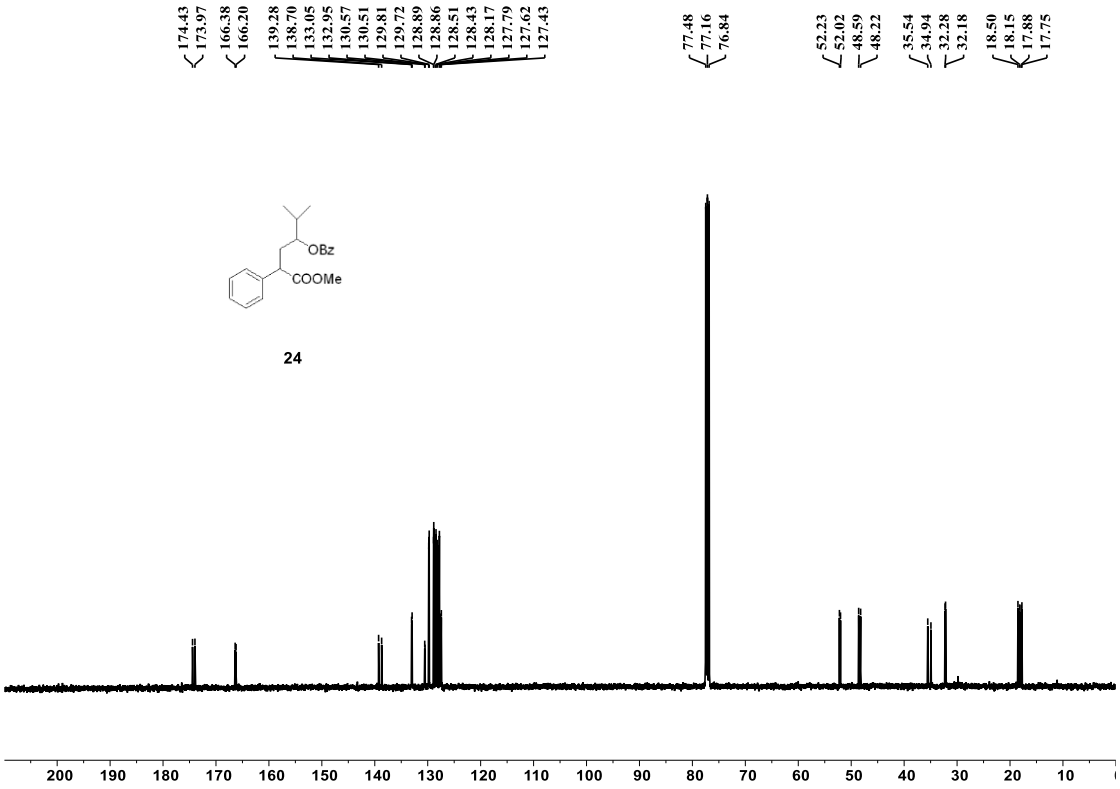
23

^{1}H NMR (400 MHz, $CDCl_3$)

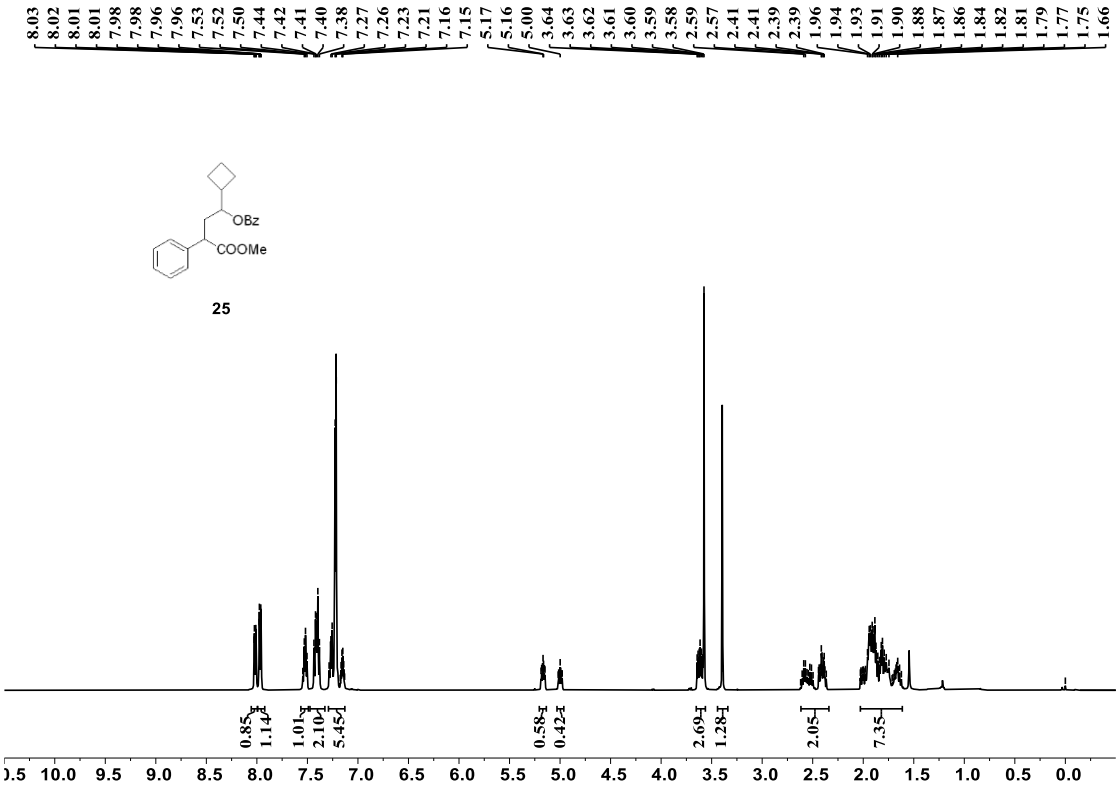


24

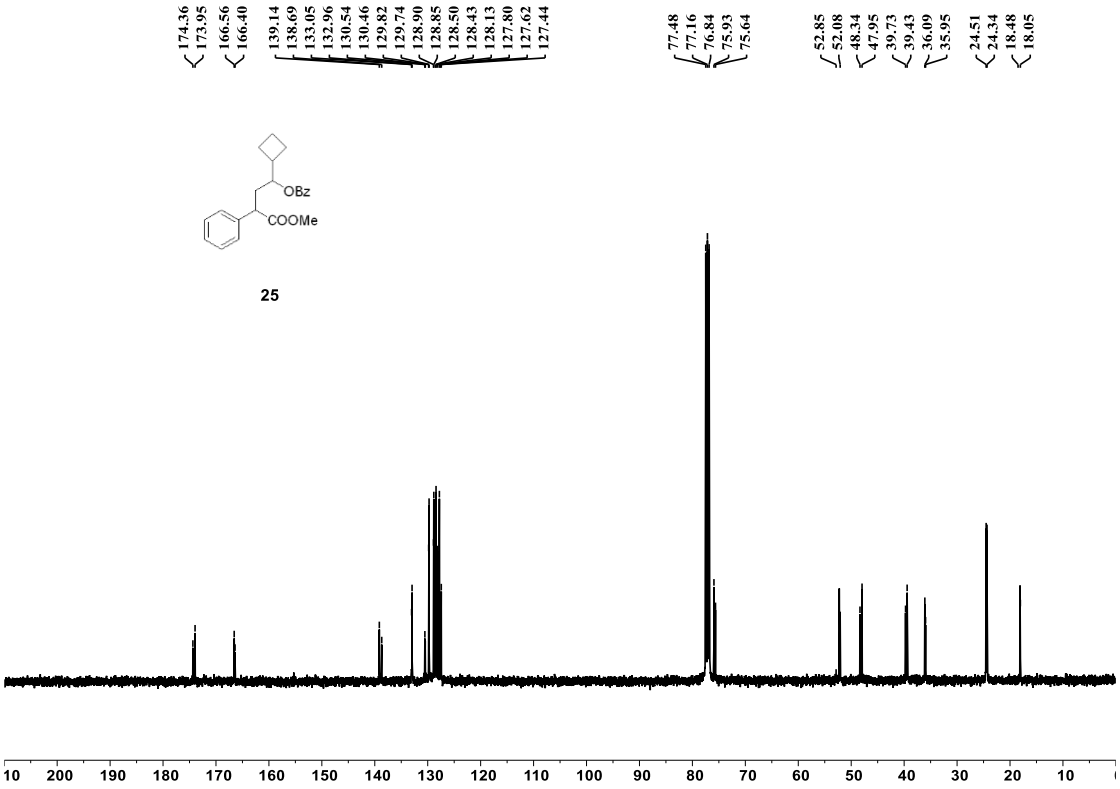
^{13}C NMR (101 MHz, $CDCl_3$)



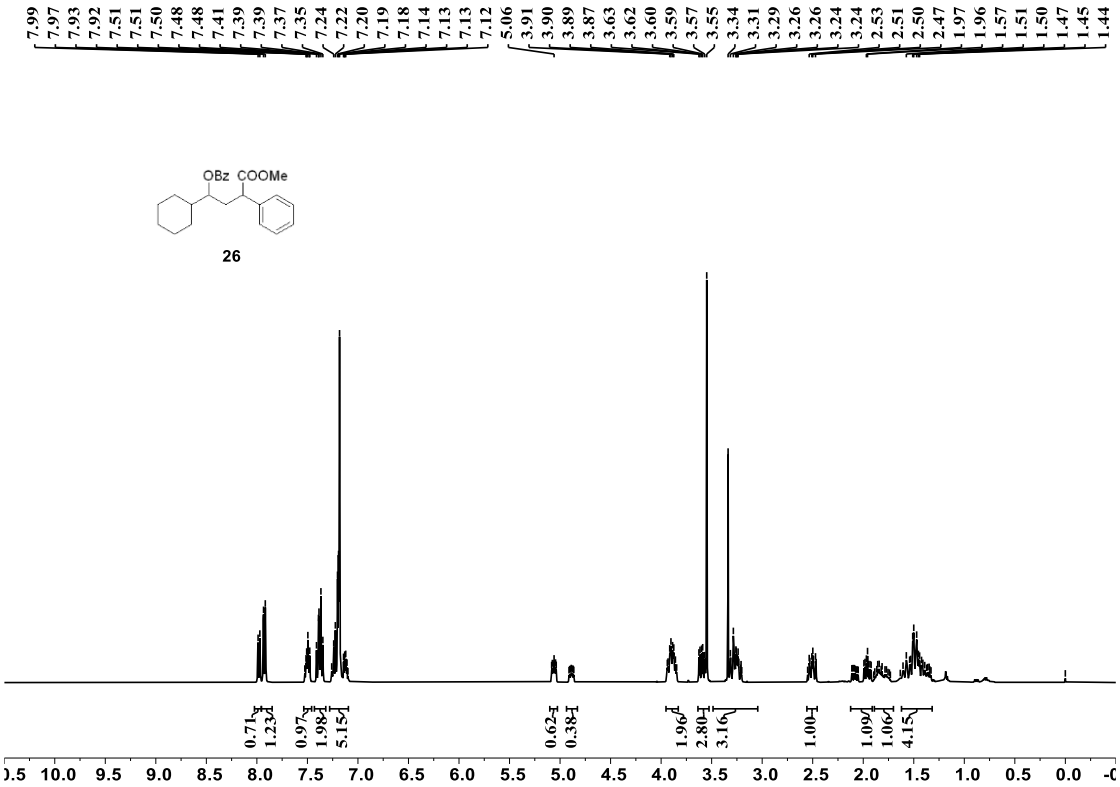
^{1}H NMR (500 MHz, $CDCl_3$)



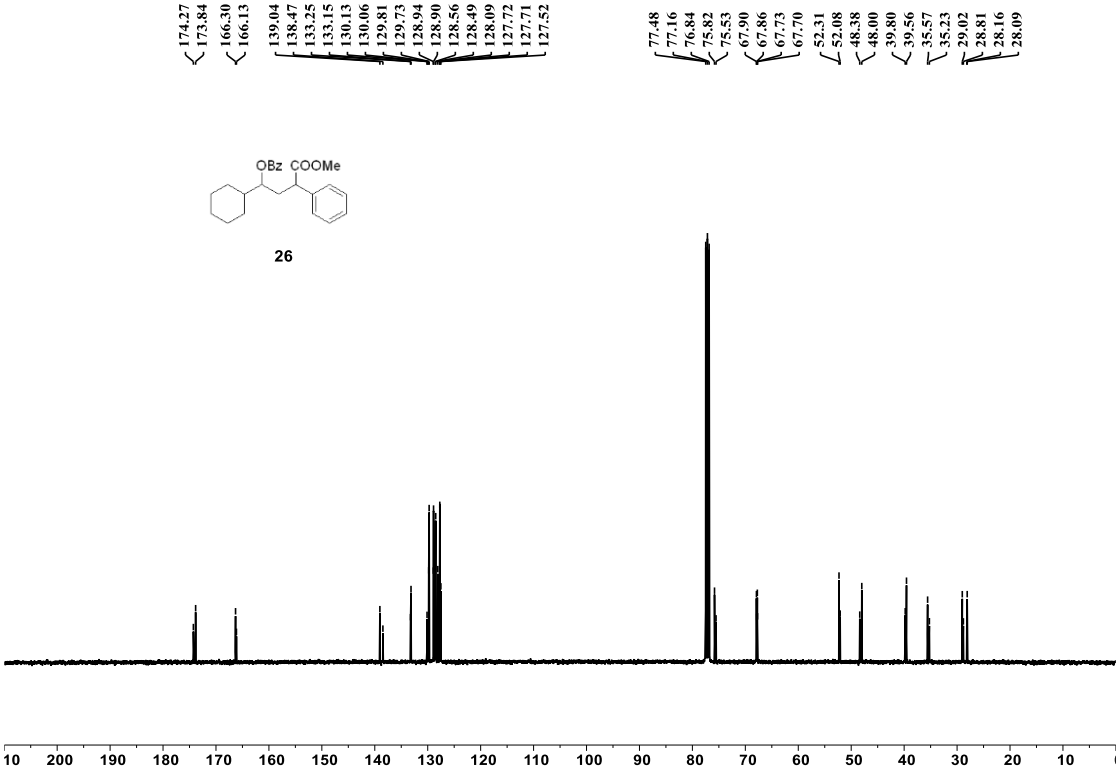
^{13}C NMR (101 MHz, $CDCl_3$)



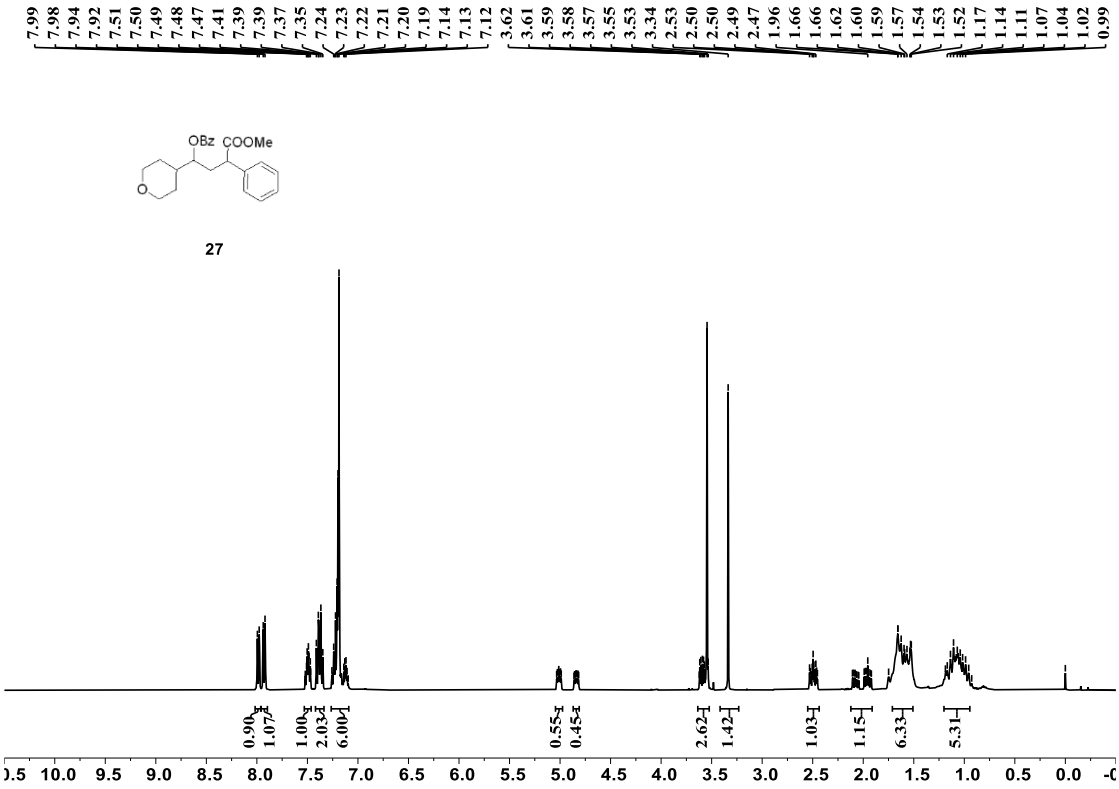
^{1}H NMR (400 MHz, $CDCl_3$)



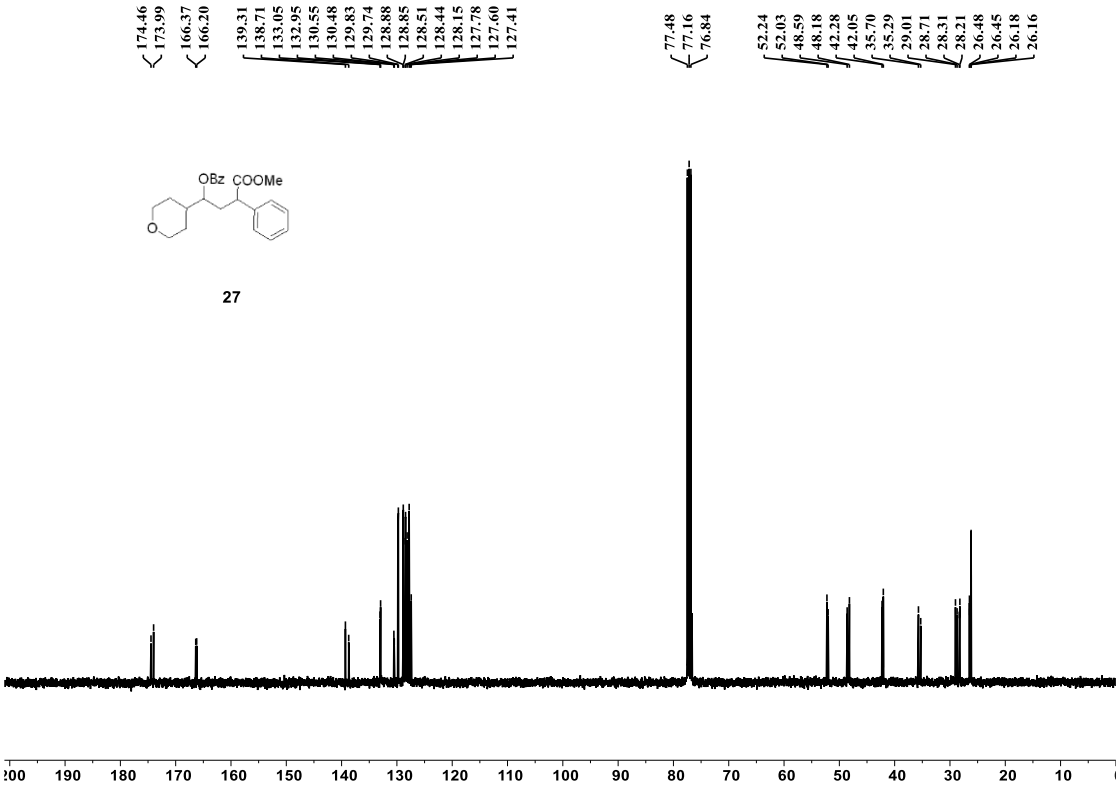
^{13}C NMR (101 MHz, $CDCl_3$)



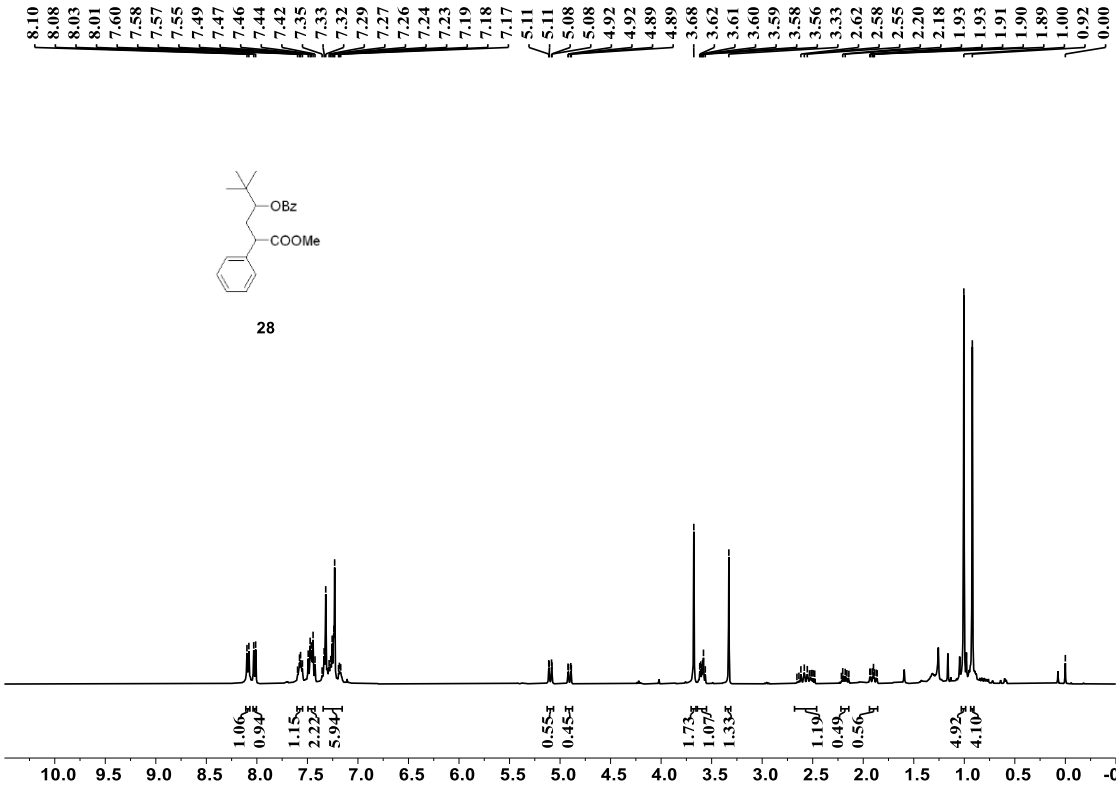
^{1}H NMR (400 MHz, $CDCl_3$)



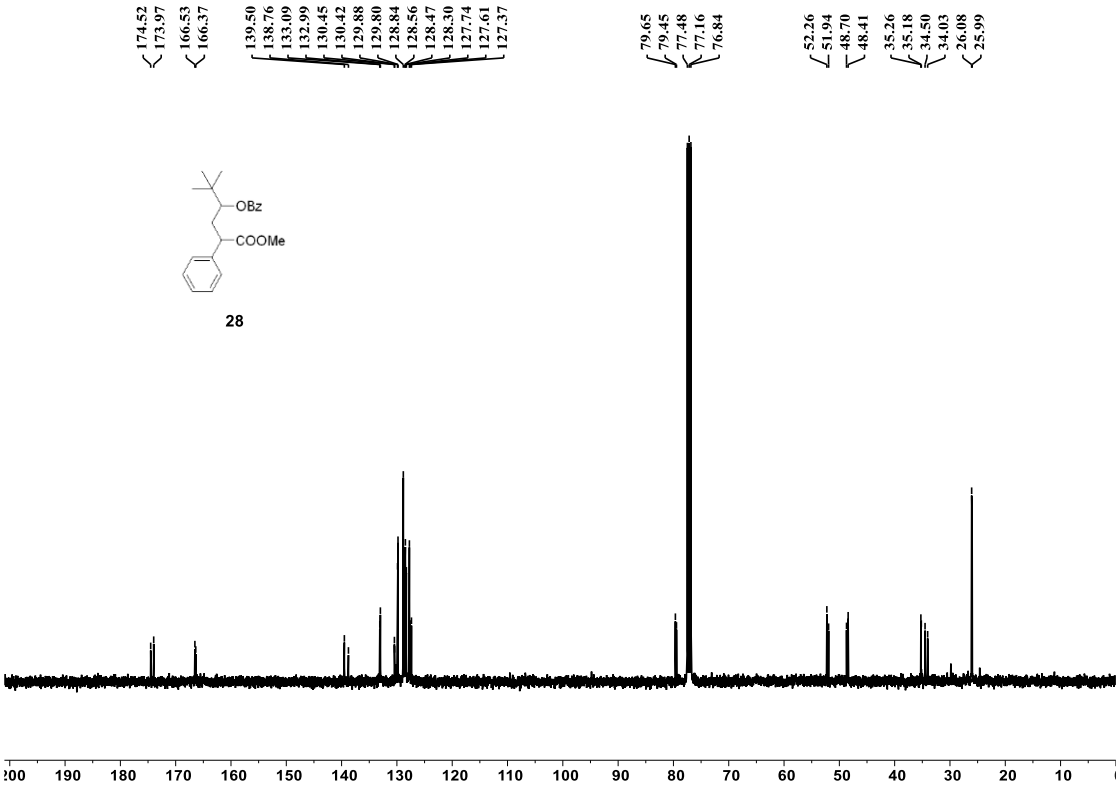
^{13}C NMR (101 MHz, $CDCl_3$)



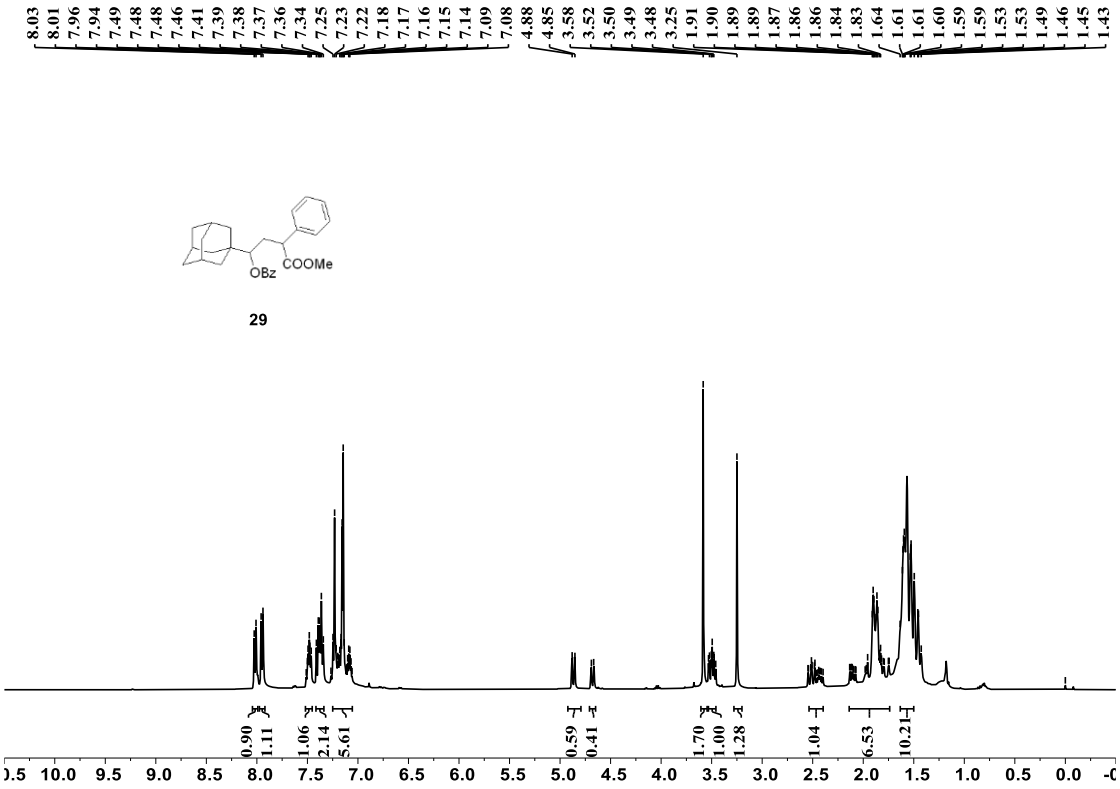
^{1}H NMR (400 MHz, $CDCl_3$)



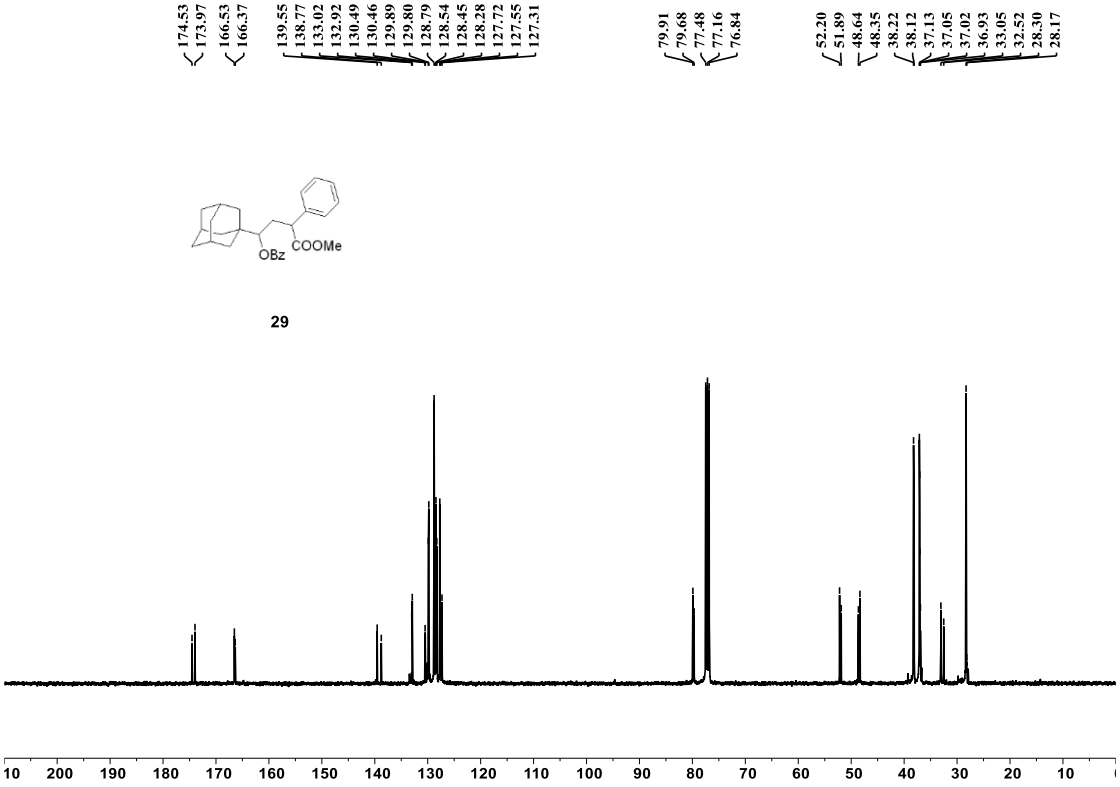
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

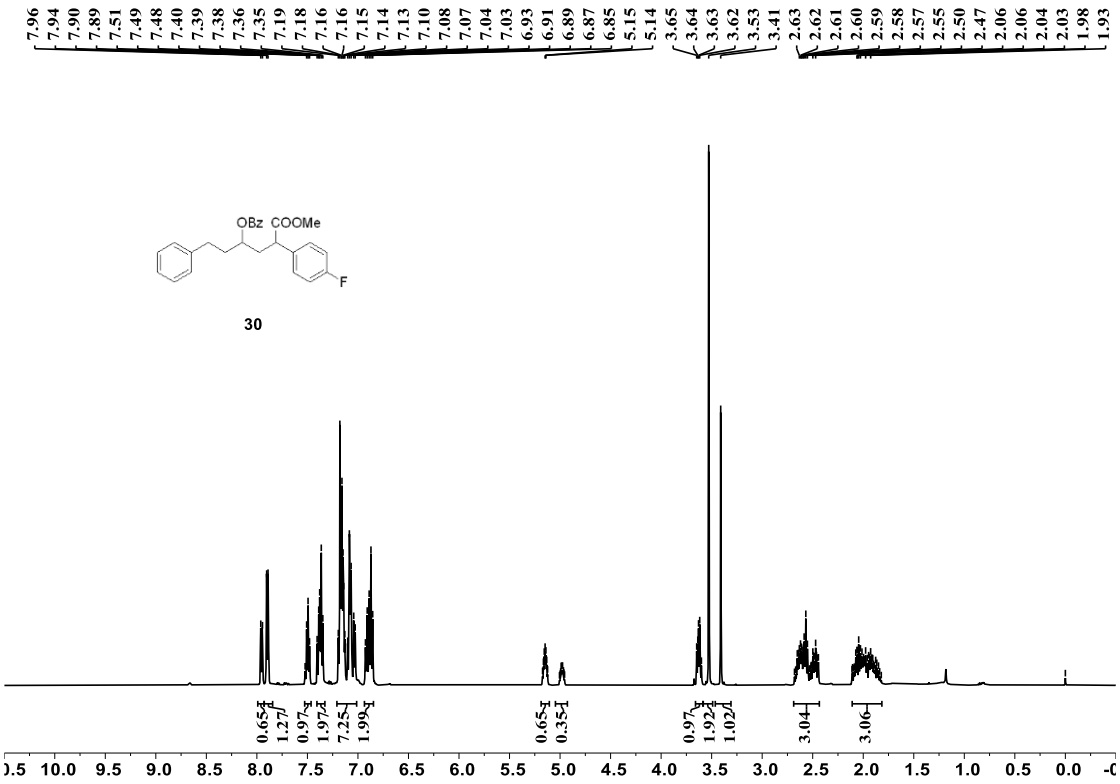


^{13}C NMR (101 MHz, $CDCl_3$)



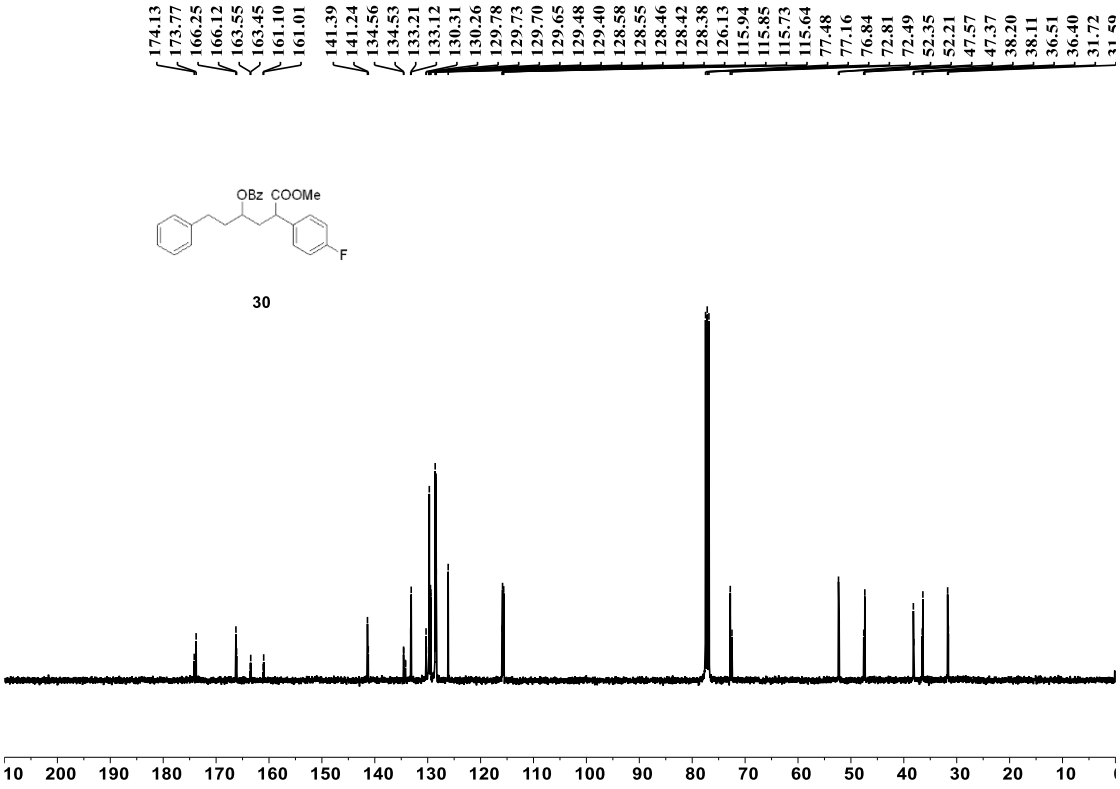
29

^{1}H NMR (500 MHz, $CDCl_3$)

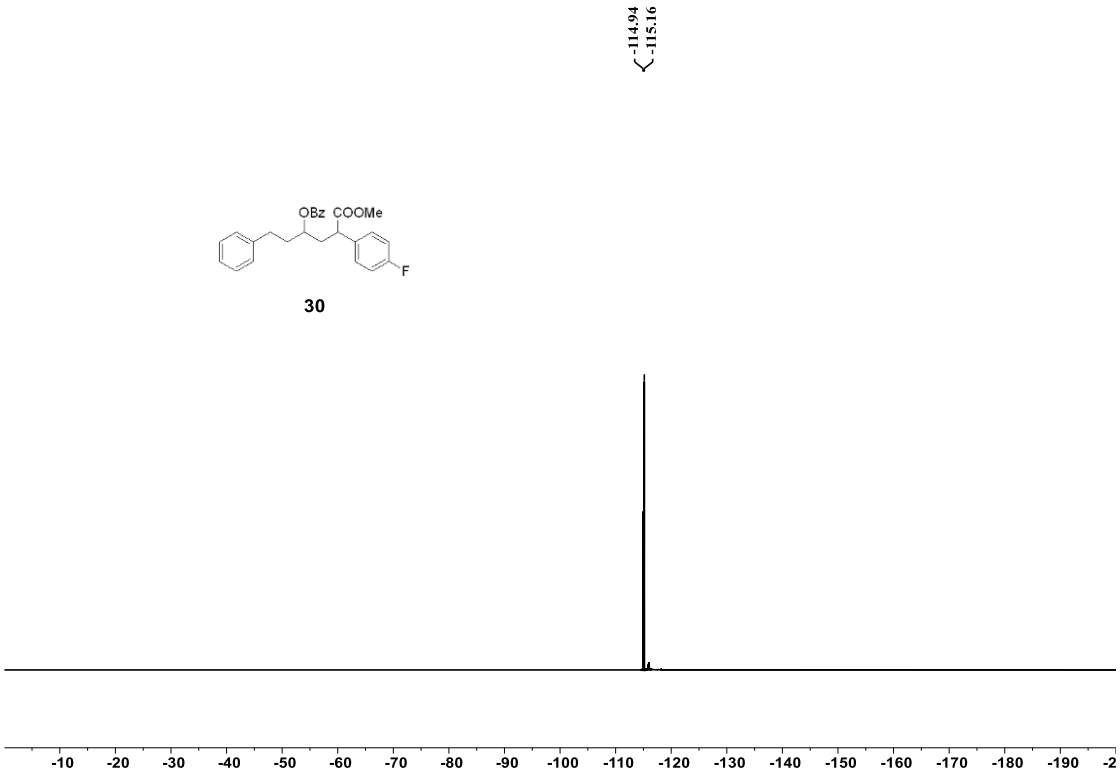


30

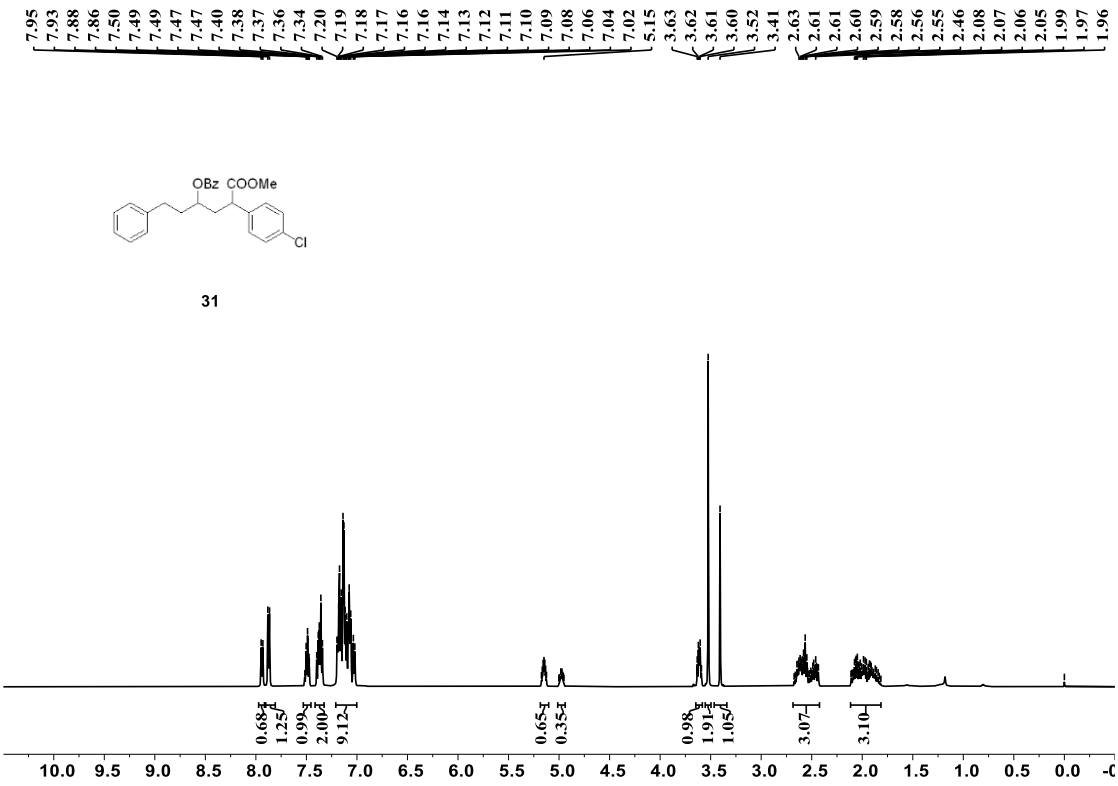
^{13}C NMR (101 MHz, $CDCl_3$)



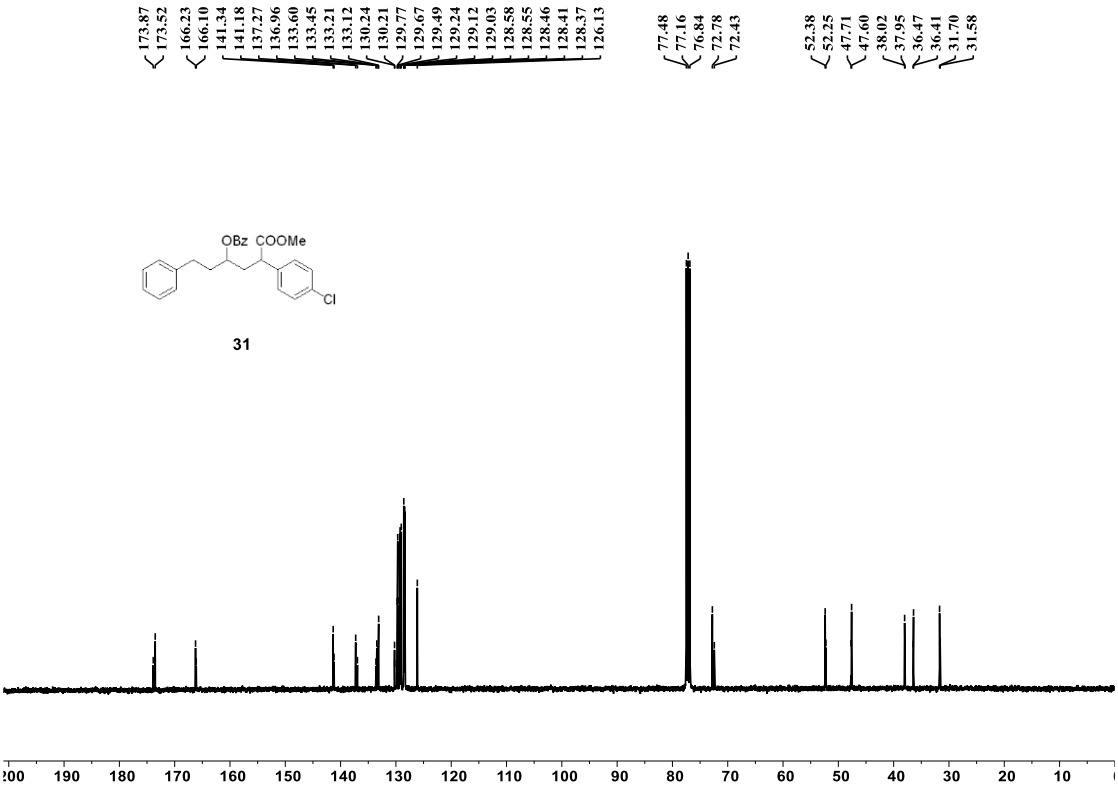
^{19}F NMR (377 MHz, $CDCl_3$)



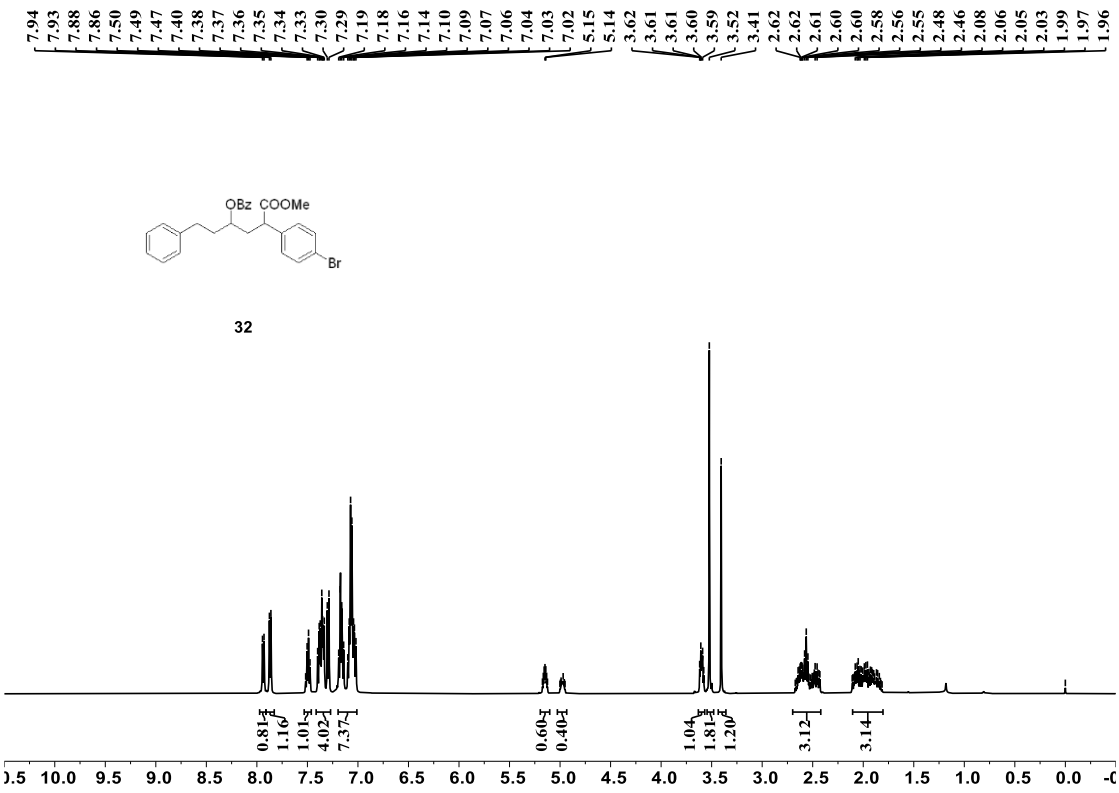
^{1}H NMR (500 MHz, $CDCl_3$)



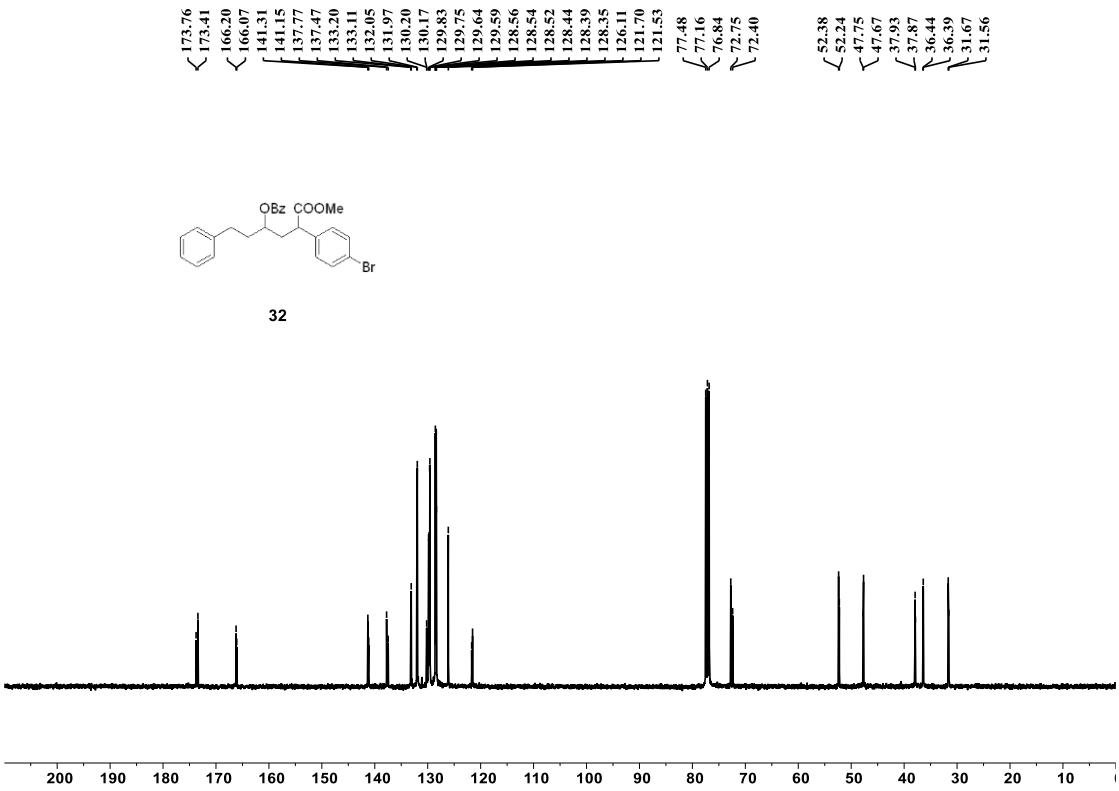
^{13}C NMR (101 MHz, $CDCl_3$)



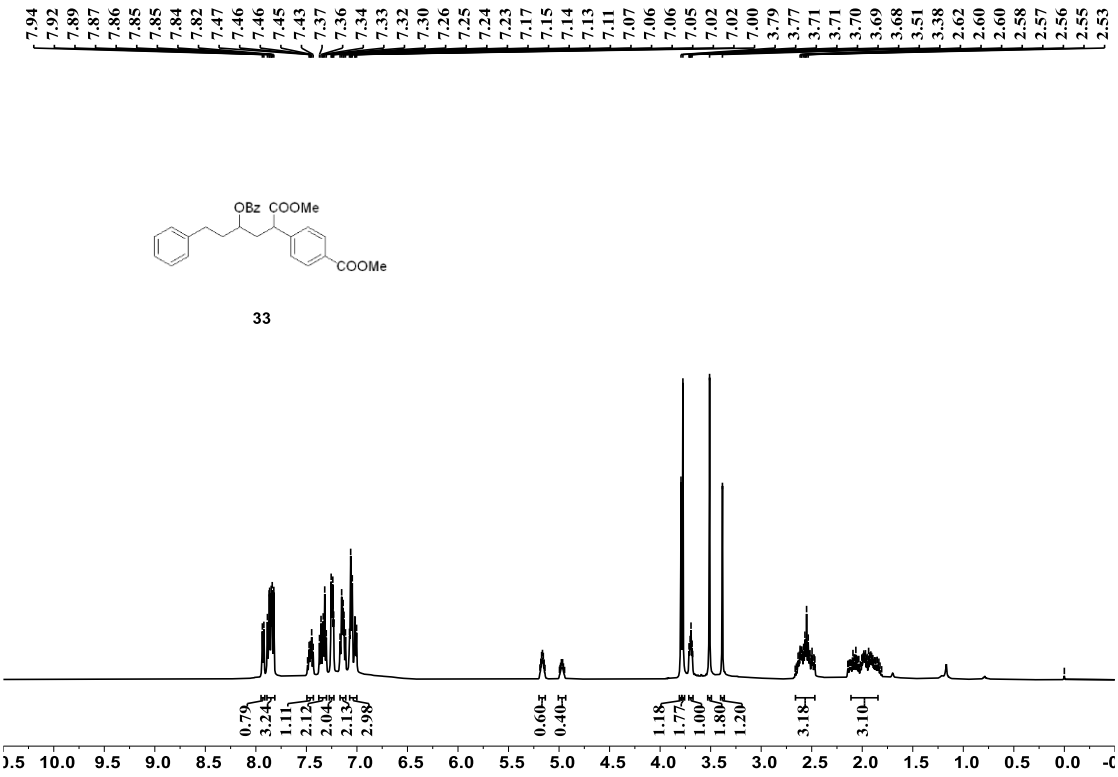
^{1}H NMR (500 MHz, $CDCl_3$)



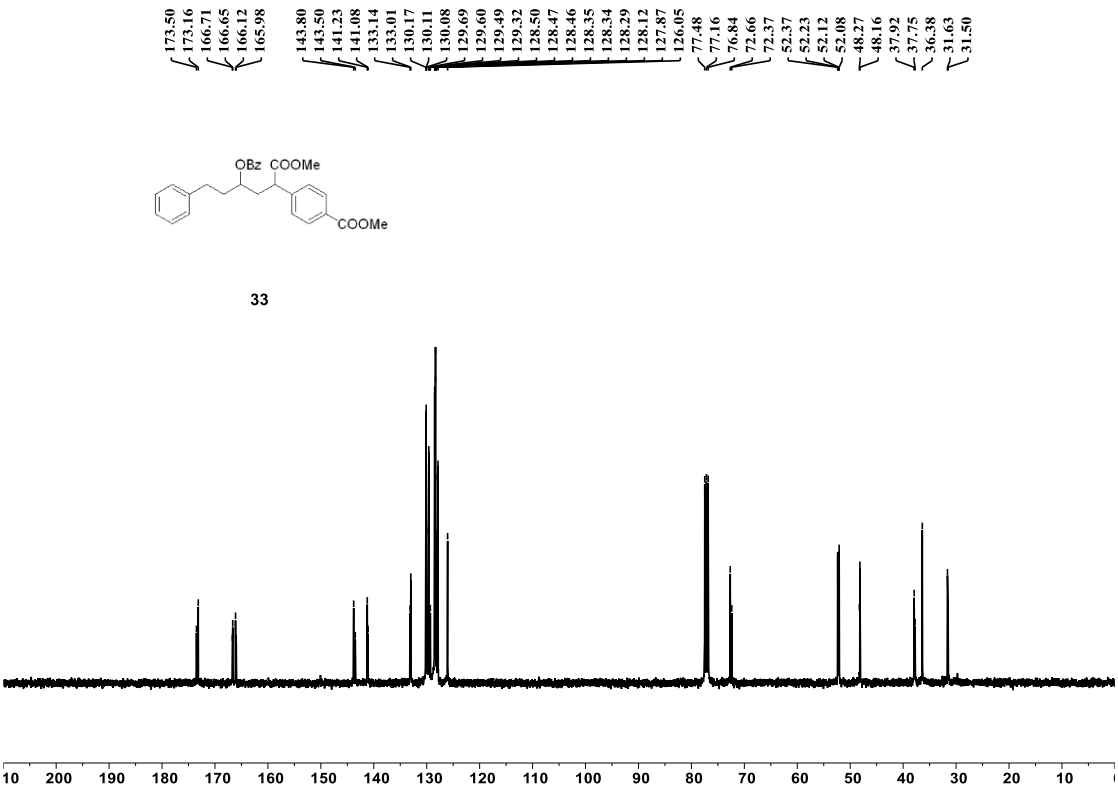
^{13}C NMR (101 MHz, $CDCl_3$)



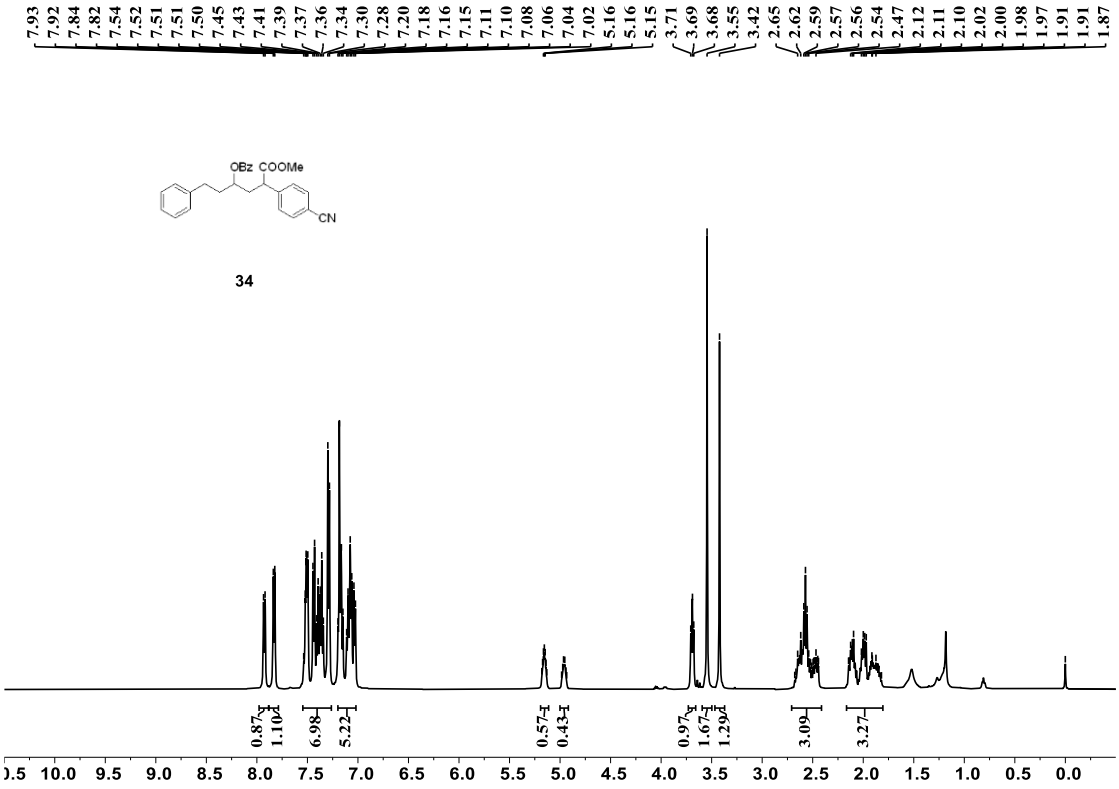
^{1}H NMR (500 MHz, $CDCl_3$)



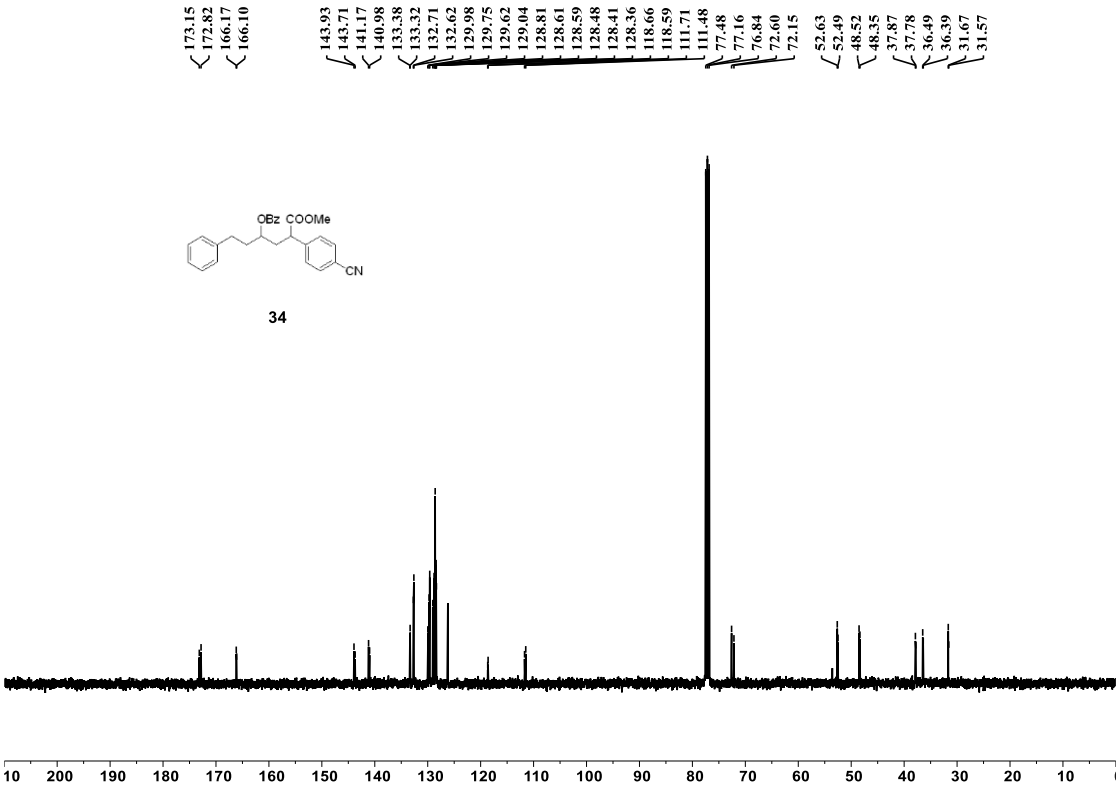
^{13}C NMR (101 MHz, $CDCl_3$)



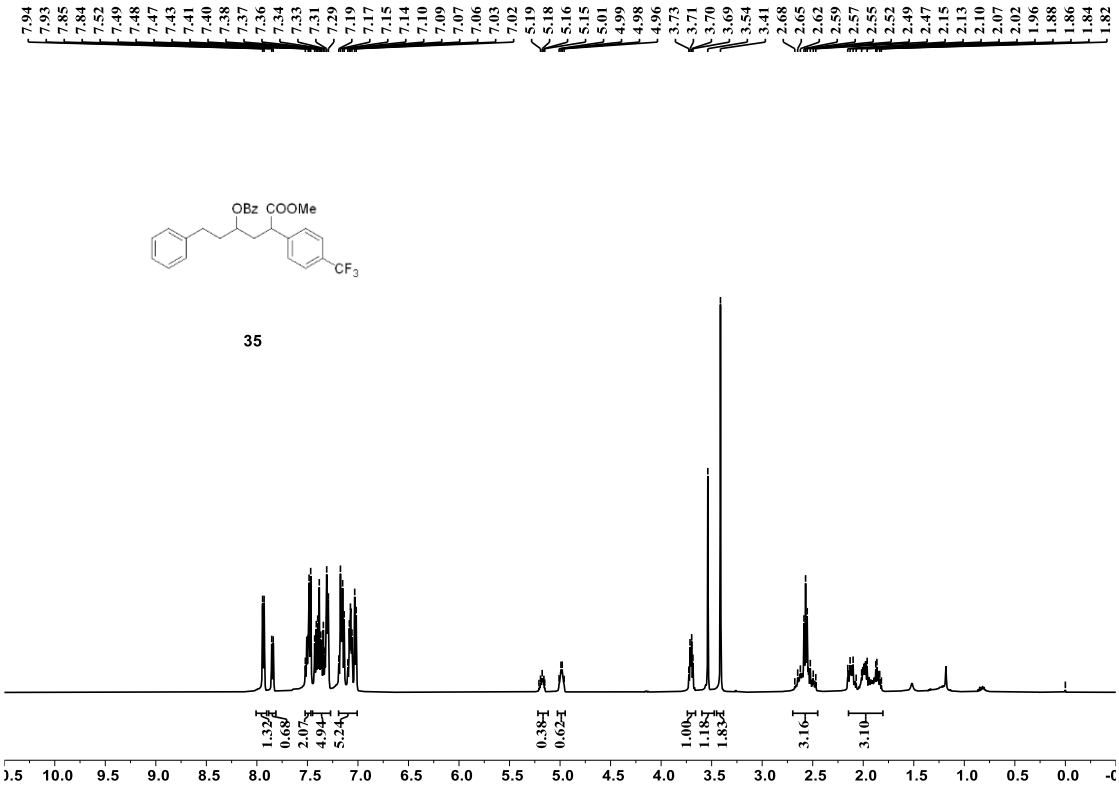
^{1}H NMR (400 MHz, $CDCl_3$)



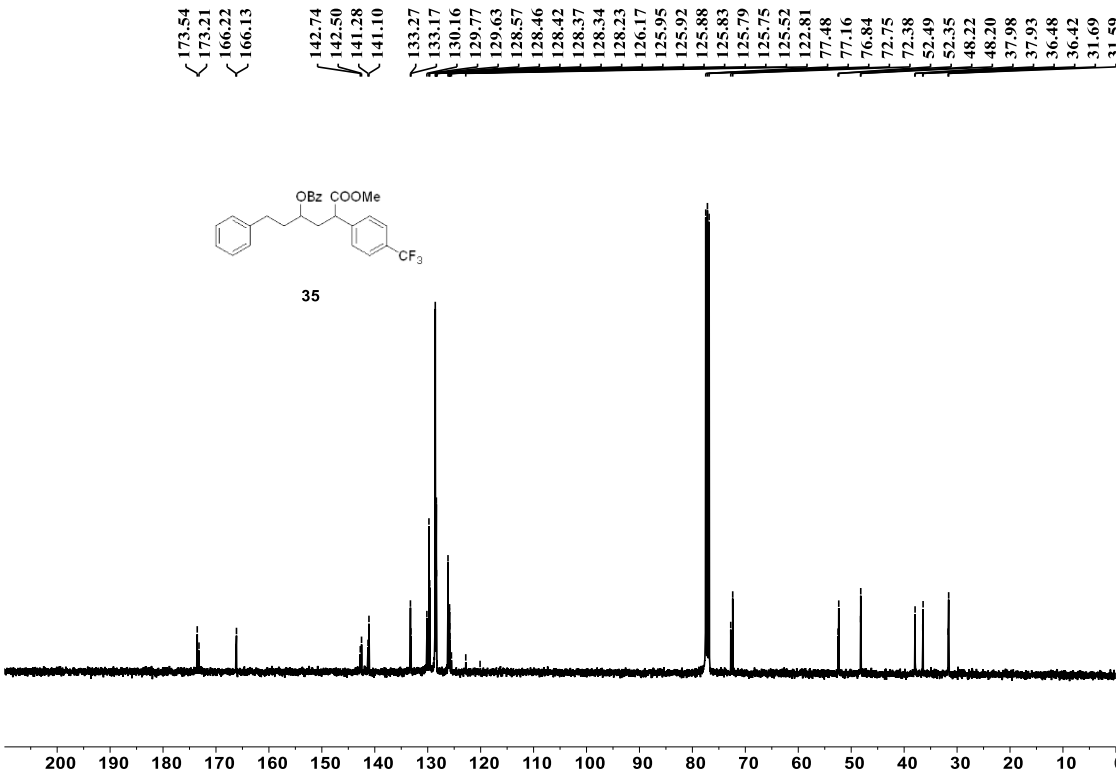
^{13}C NMR (101 MHz, $CDCl_3$)



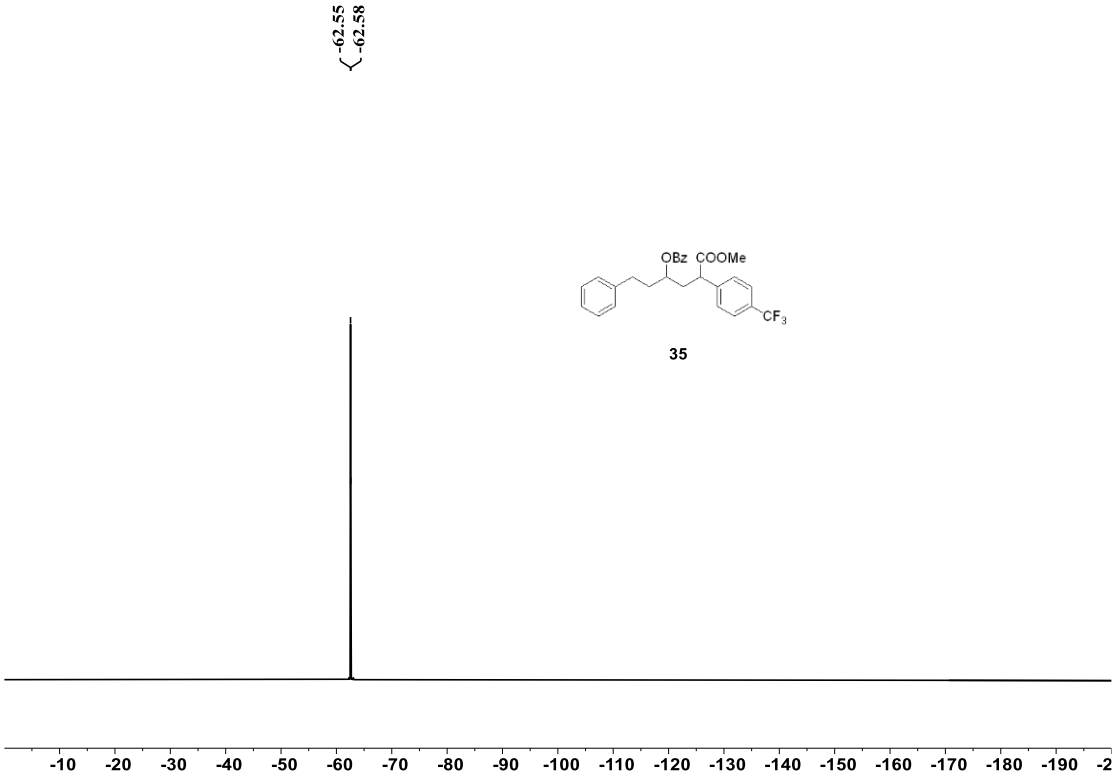
^{1}H NMR (500 MHz, $CDCl_3$)



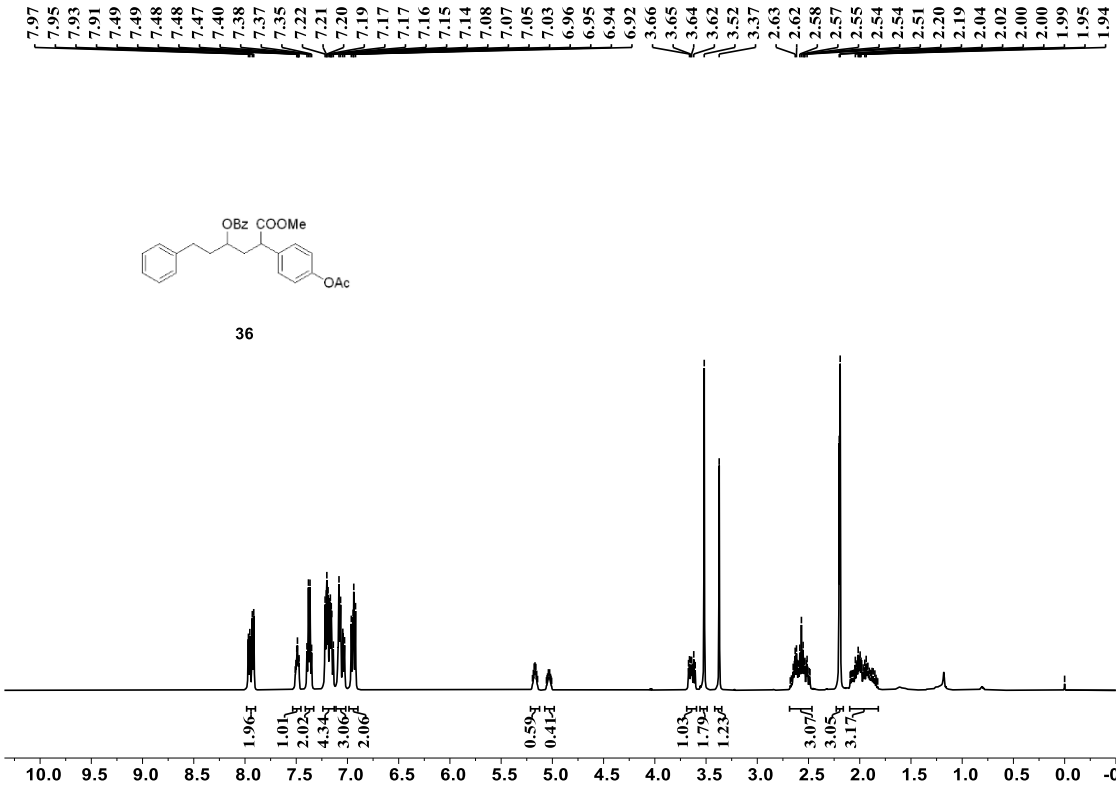
^{13}C NMR (101 MHz, $CDCl_3$)



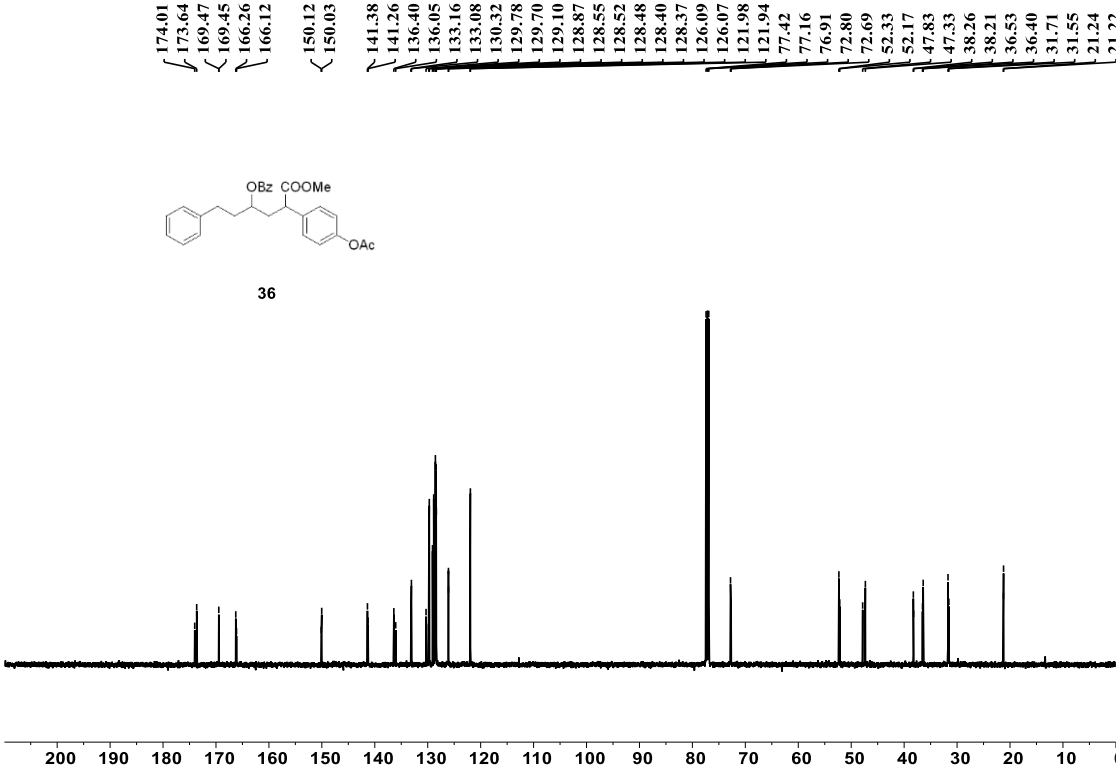
^{19}F NMR (377 MHz, $CDCl_3$)



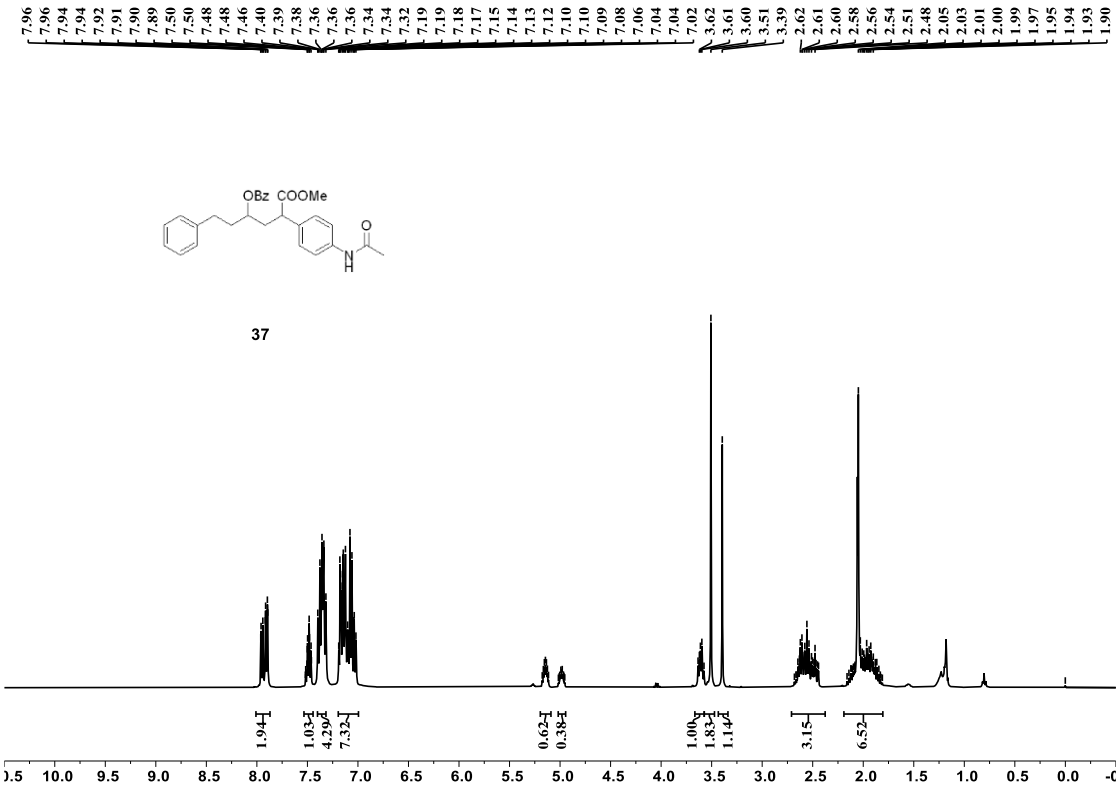
^{1}H NMR (500 MHz, $CDCl_3$)



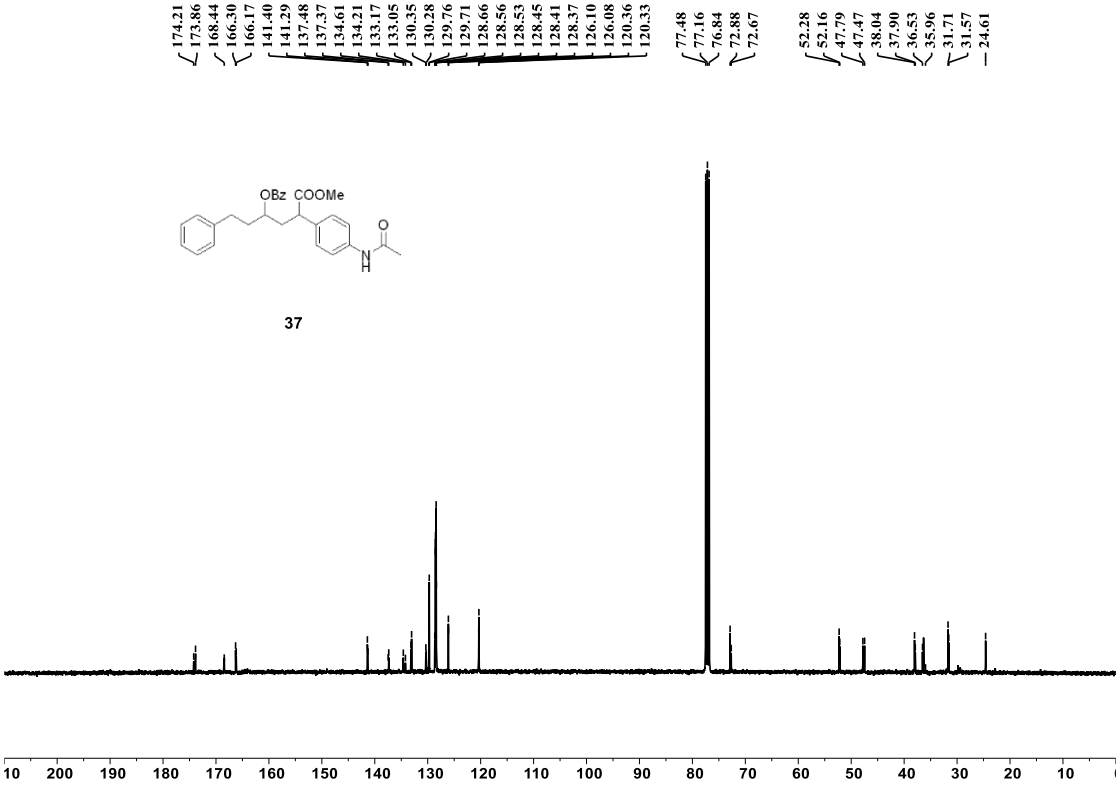
^{13}C NMR (126 MHz, $CDCl_3$)



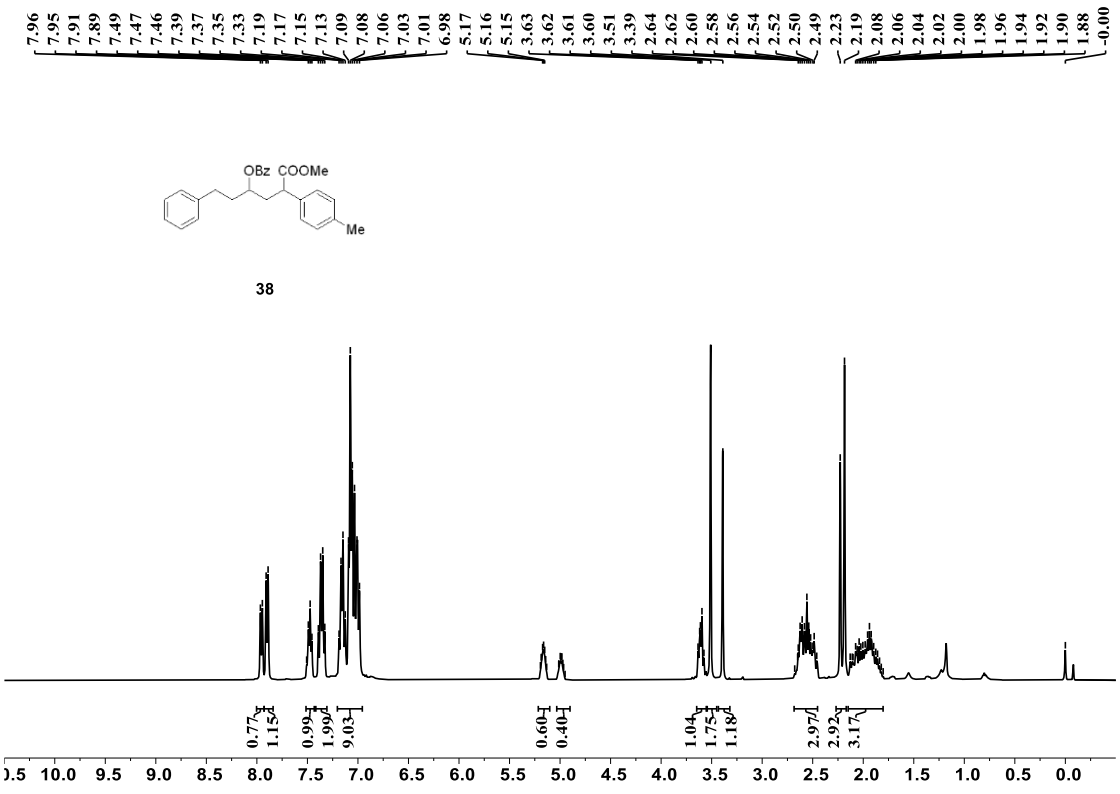
^{1}H NMR (400 MHz, $CDCl_3$)



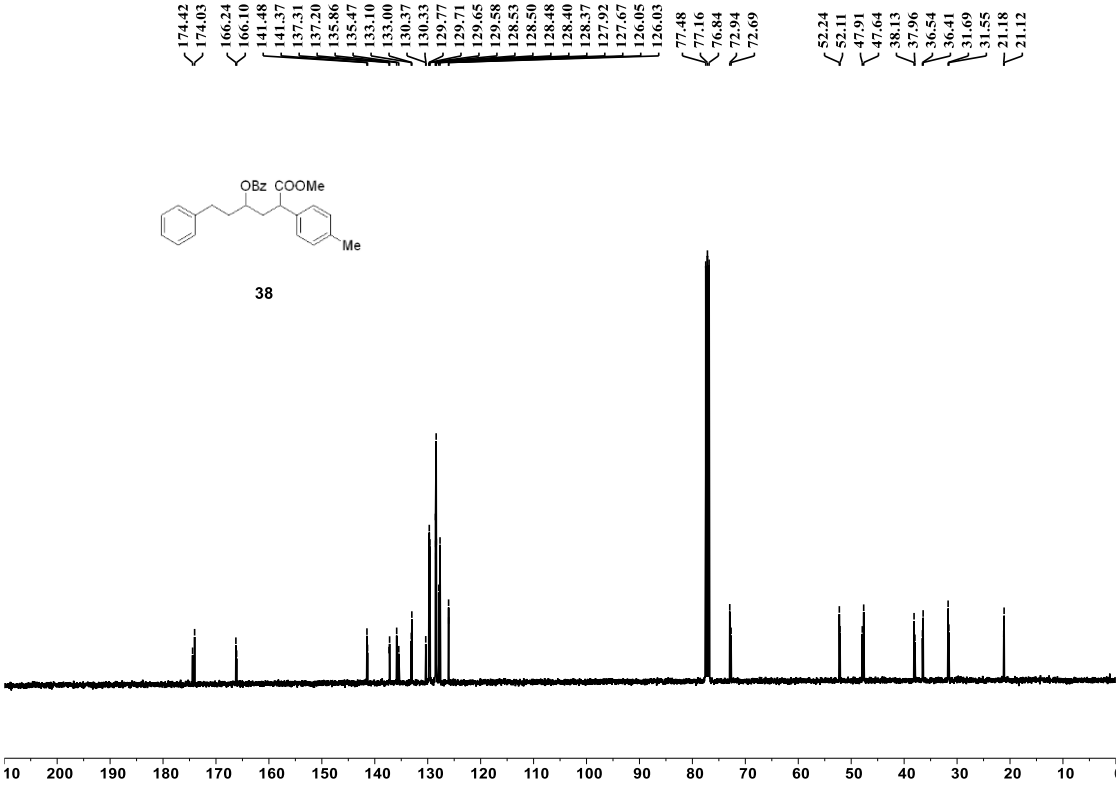
^{13}C NMR (101 MHz, $CDCl_3$)



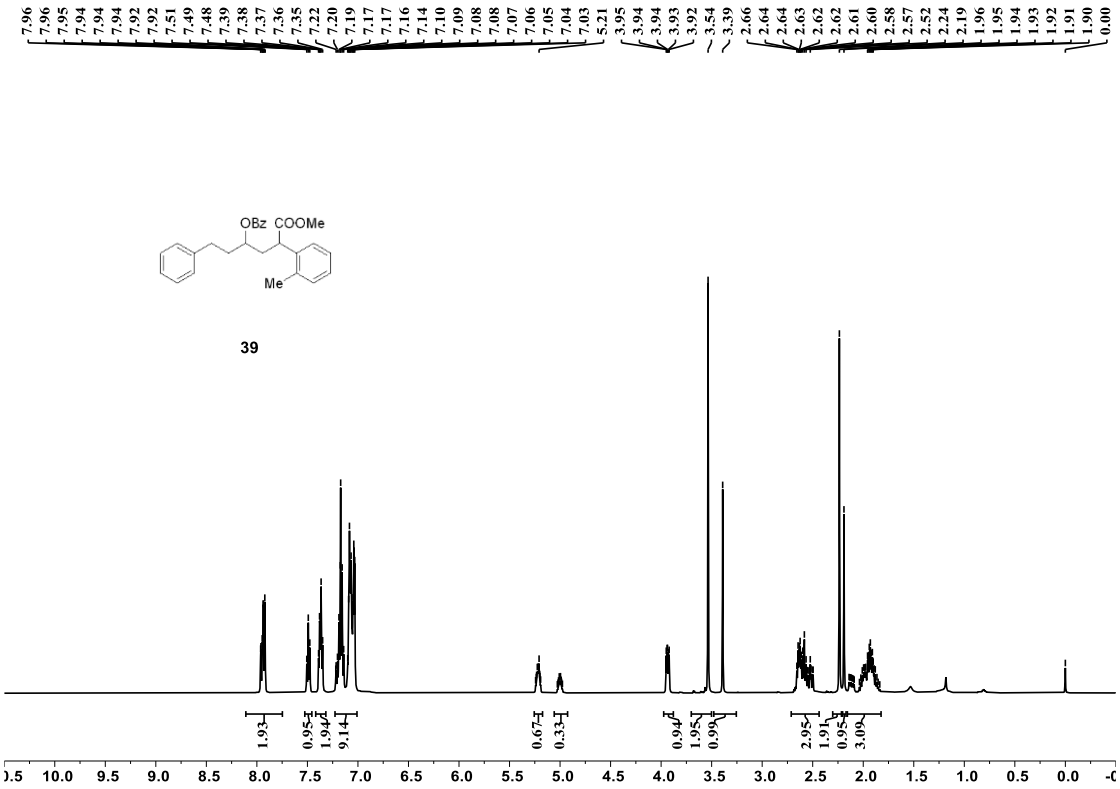
^{1}H NMR (400 MHz, $CDCl_3$)



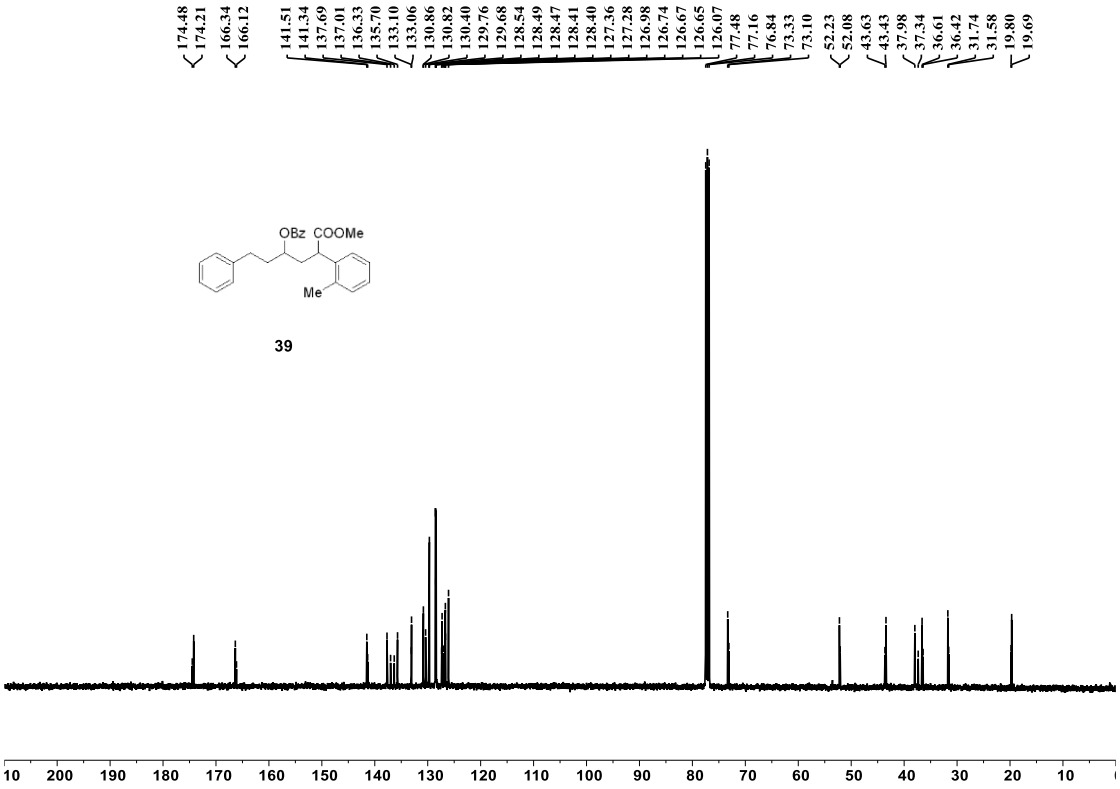
^{13}C NMR (101 MHz, $CDCl_3$)



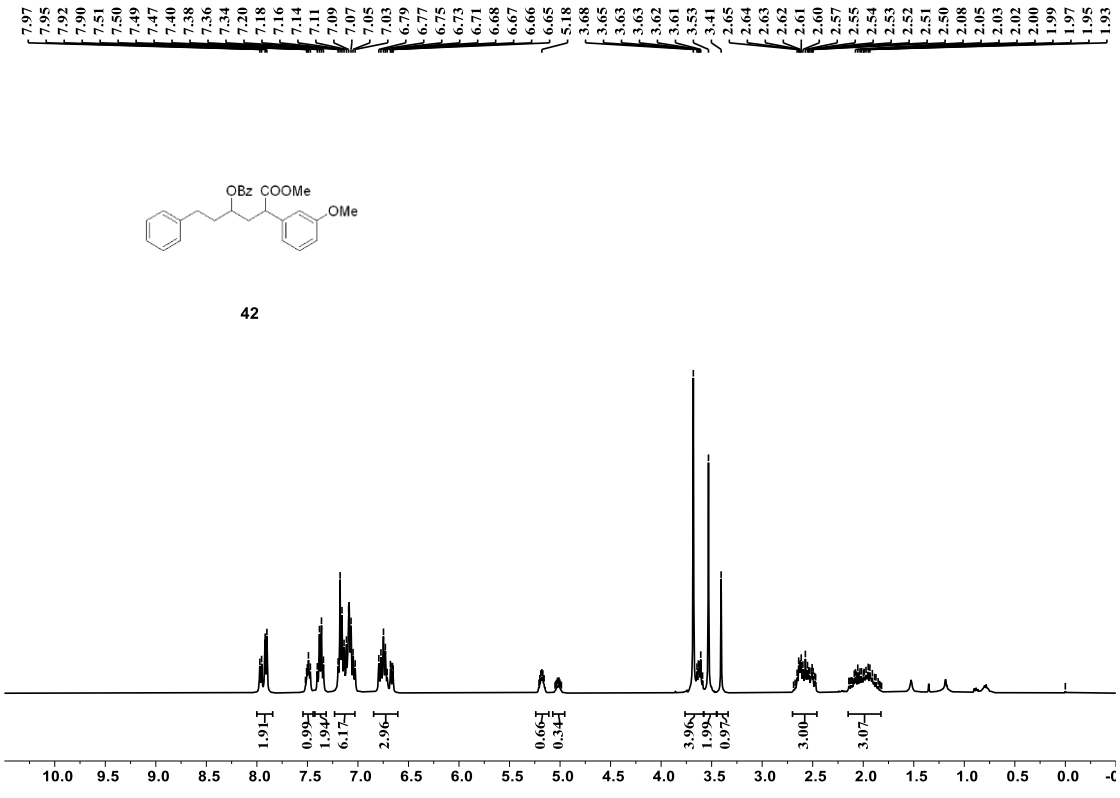
^{1}H NMR (500 MHz, $CDCl_3$)



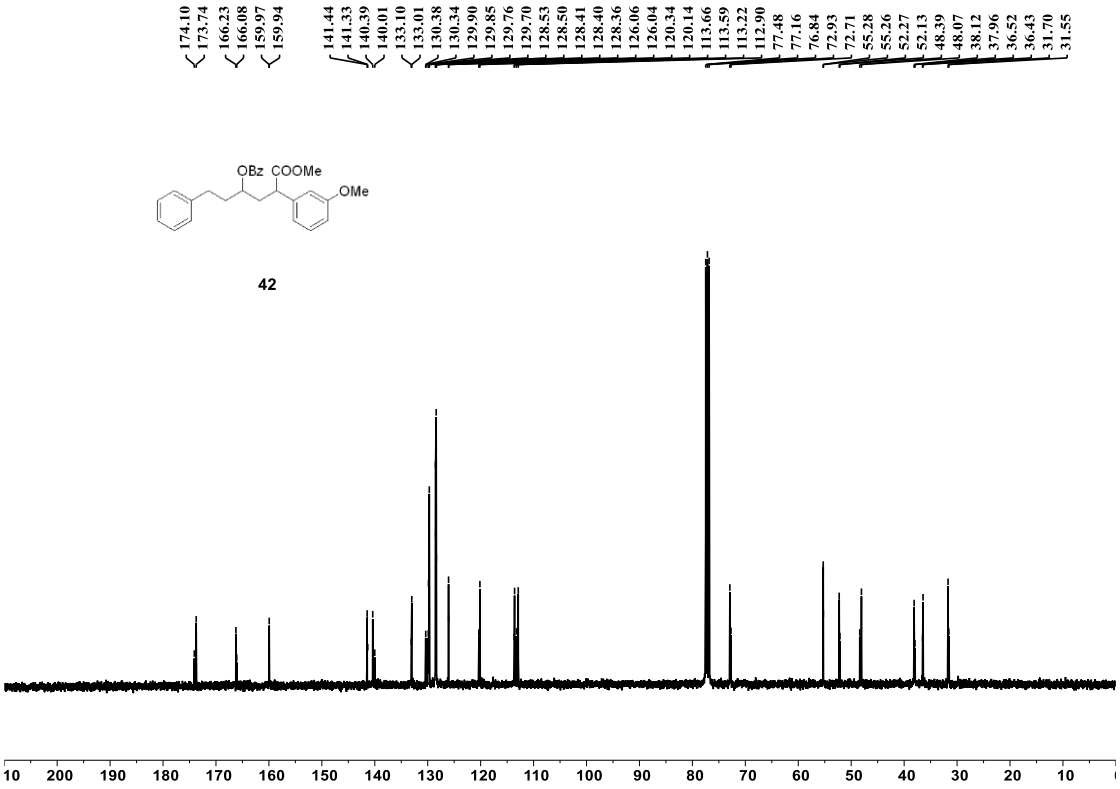
^{13}C NMR (101 MHz, $CDCl_3$)



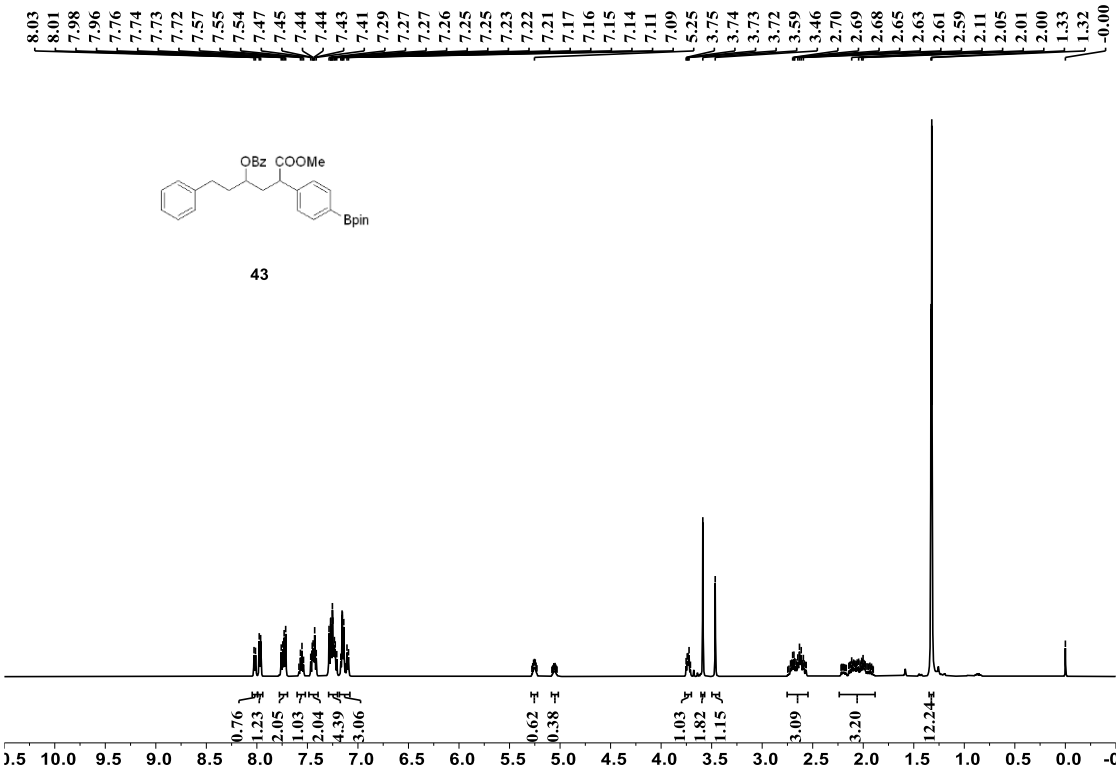
^{1}H NMR (400 MHz, $CDCl_3$)



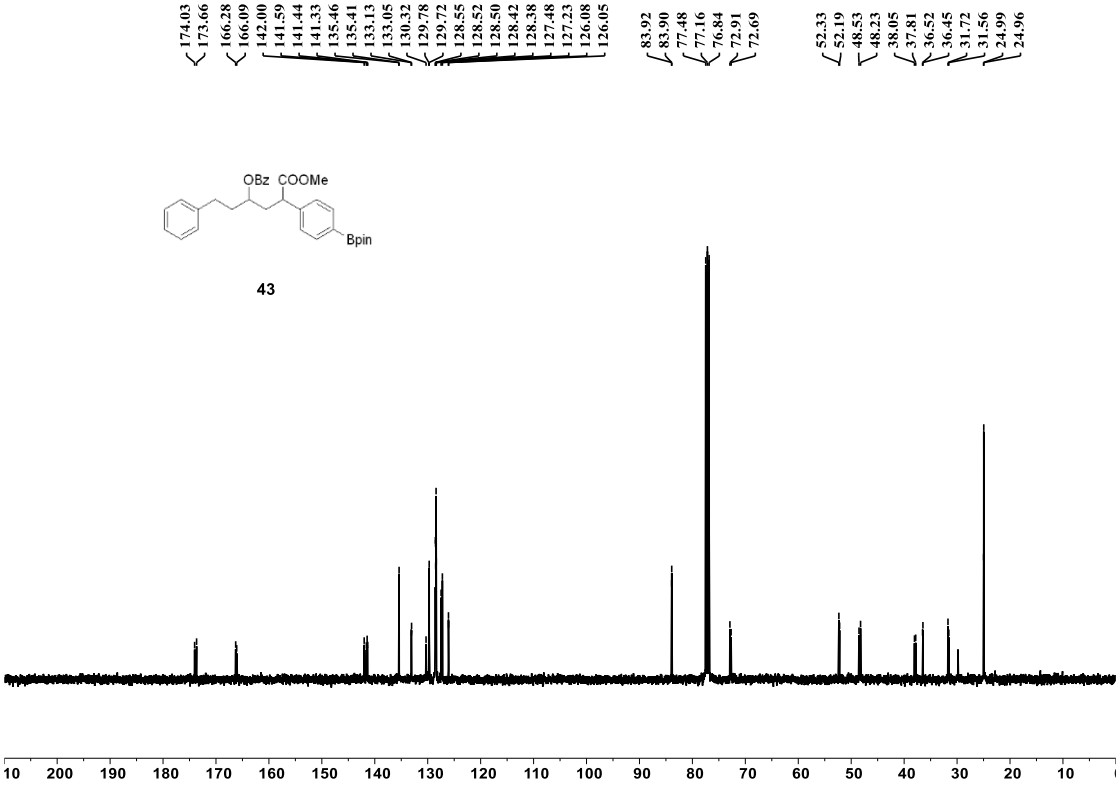
^{13}C NMR (101 MHz, $CDCl_3$)



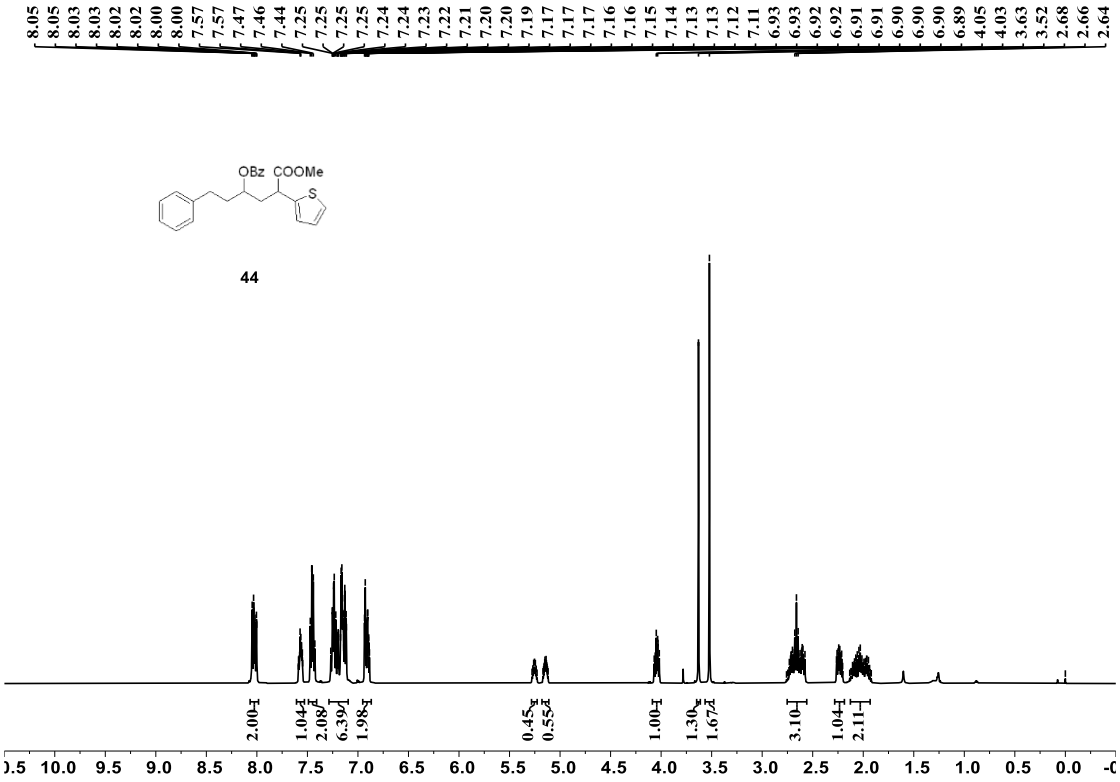
^{1}H NMR (500 MHz, $CDCl_3$)



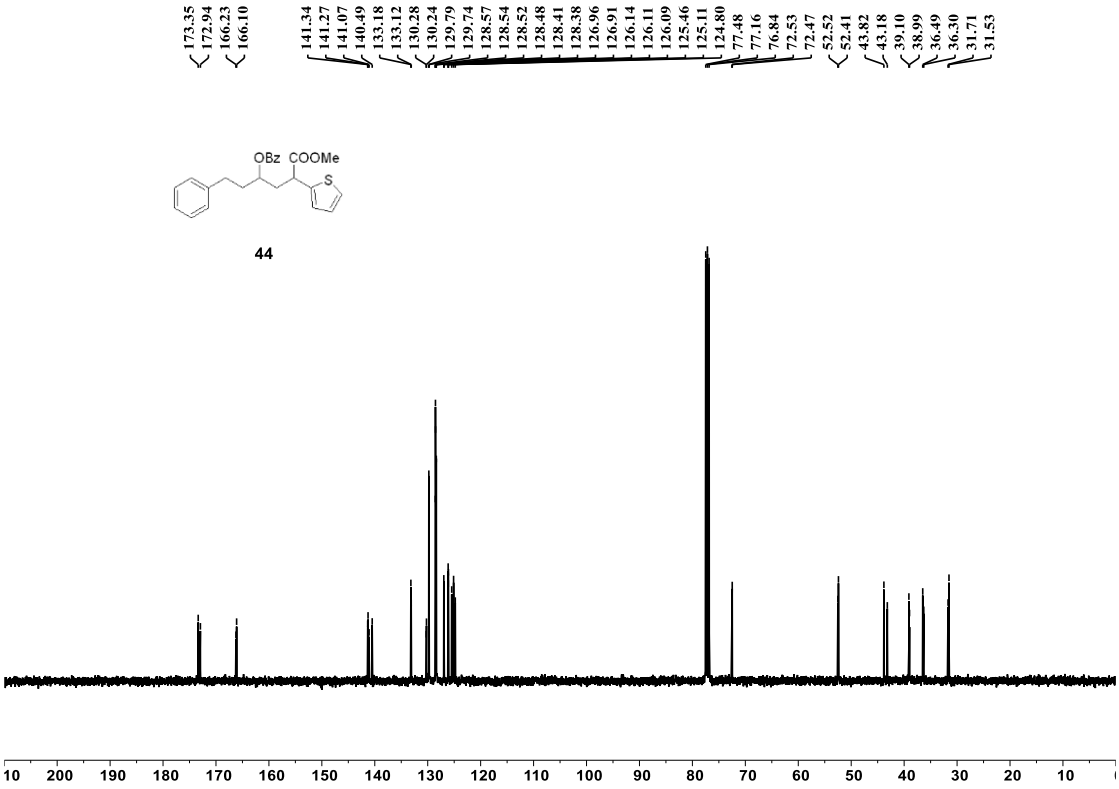
^{13}C NMR (101 MHz, $CDCl_3$)



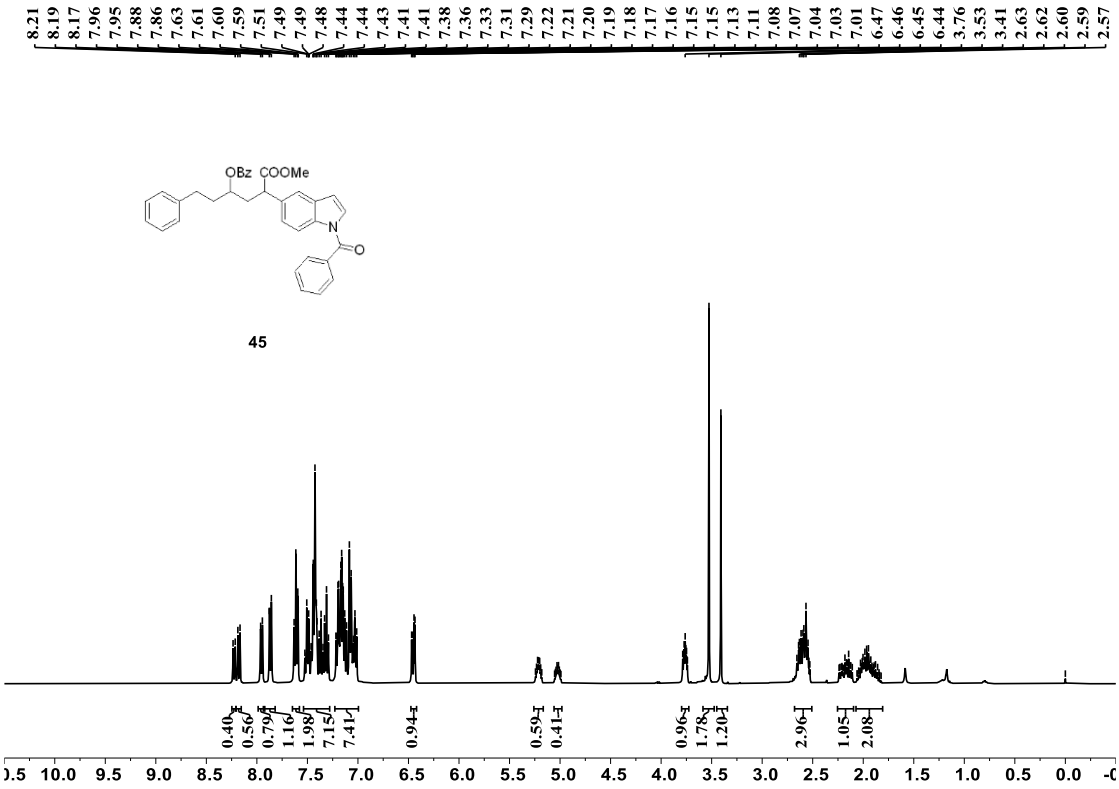
^{1}H NMR (500 MHz, $CDCl_3$)



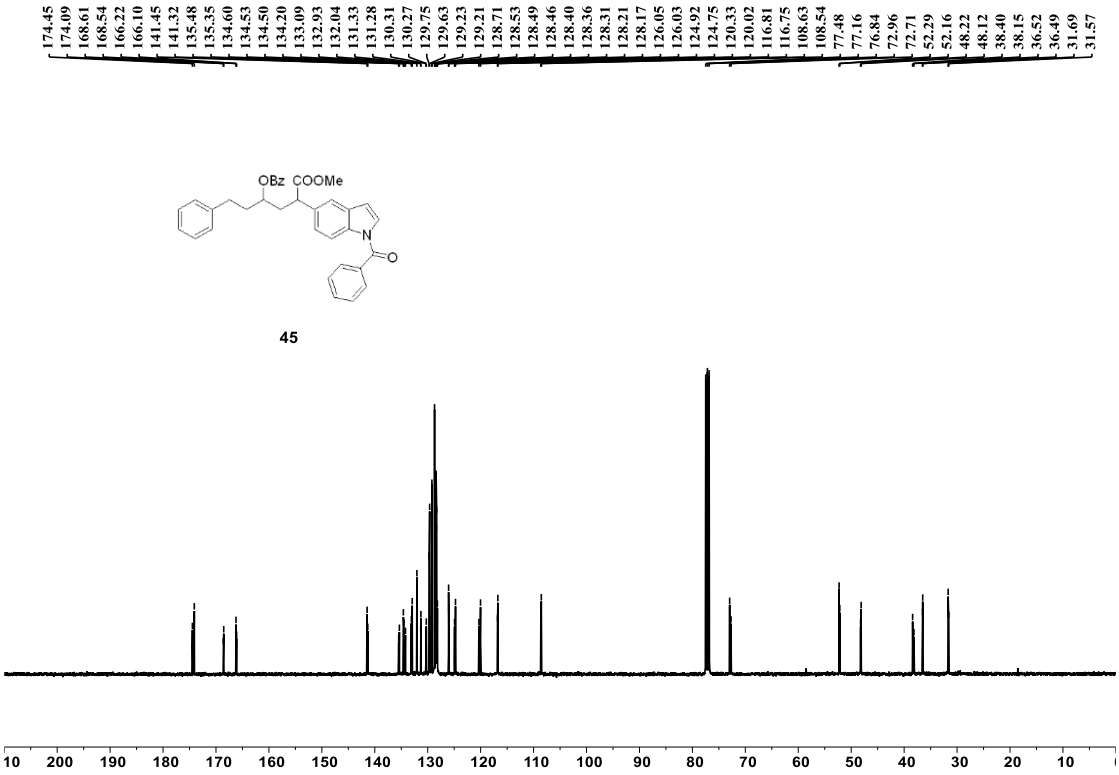
^{13}C NMR (101 MHz, $CDCl_3$)



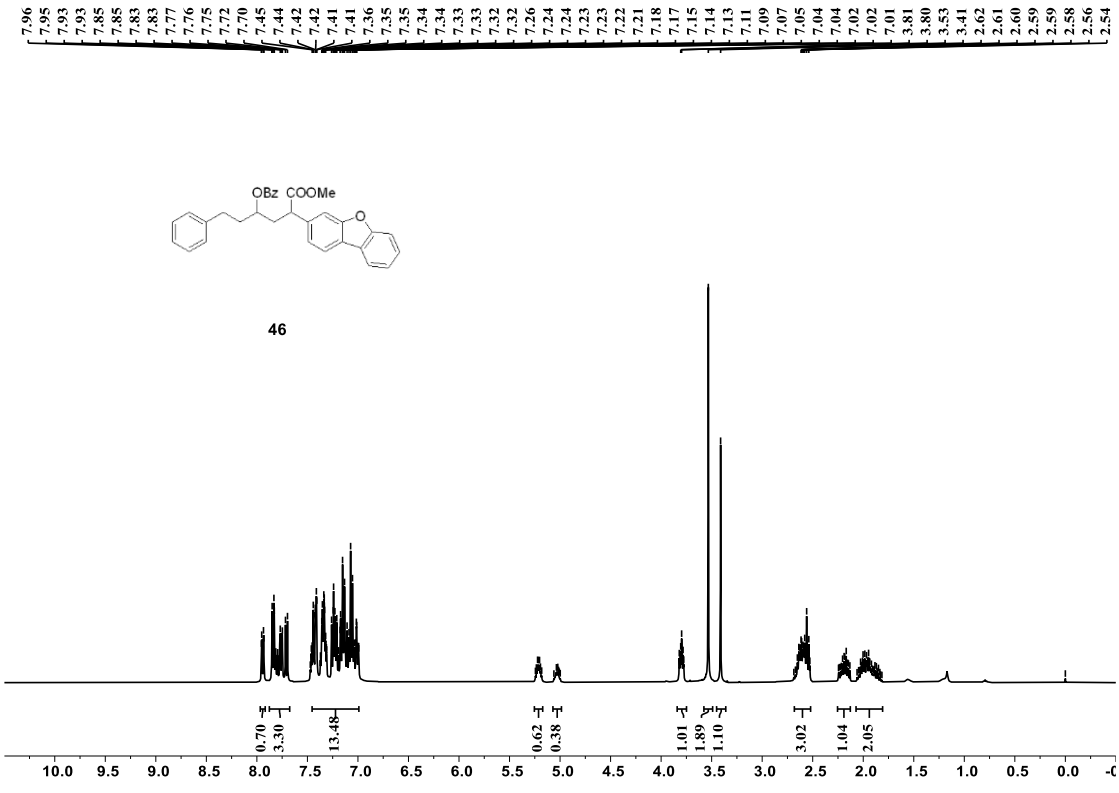
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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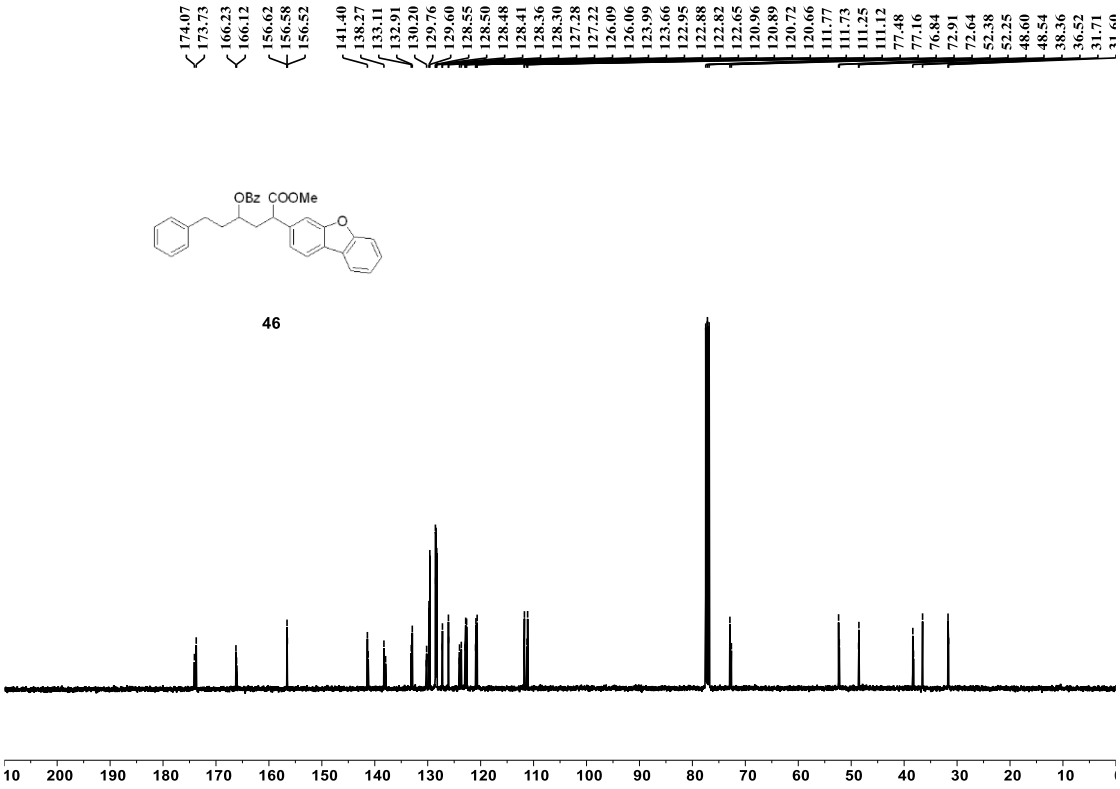
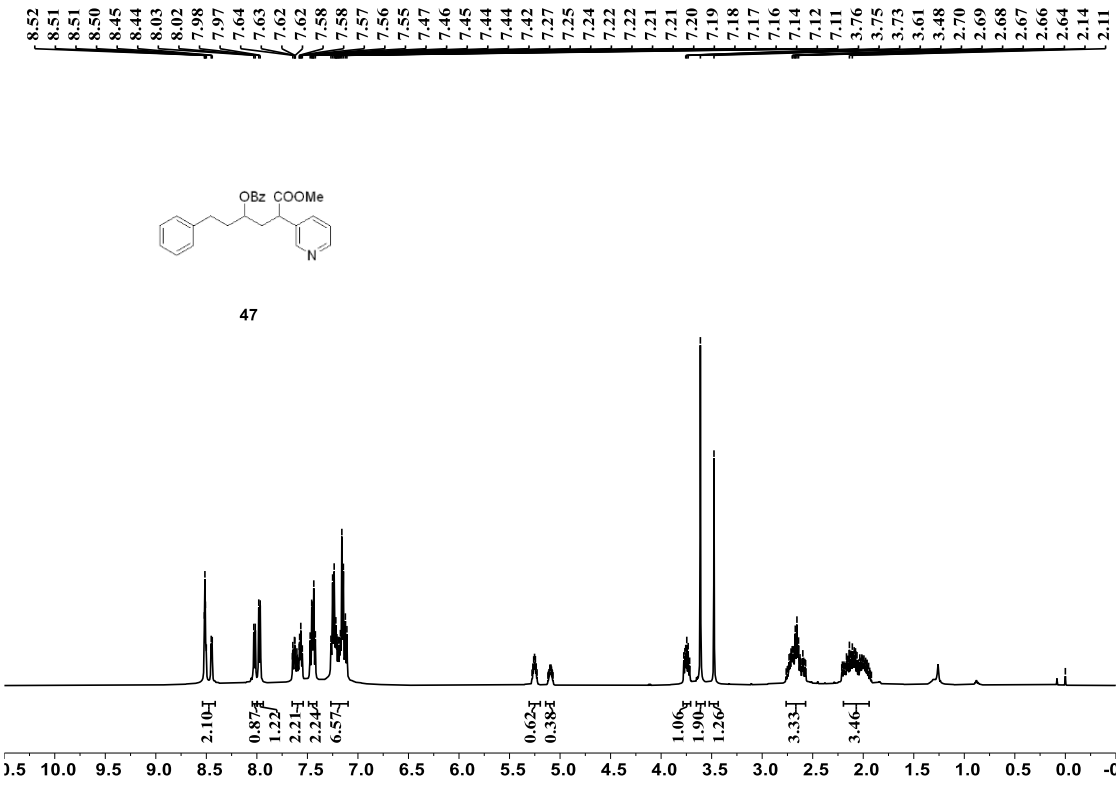
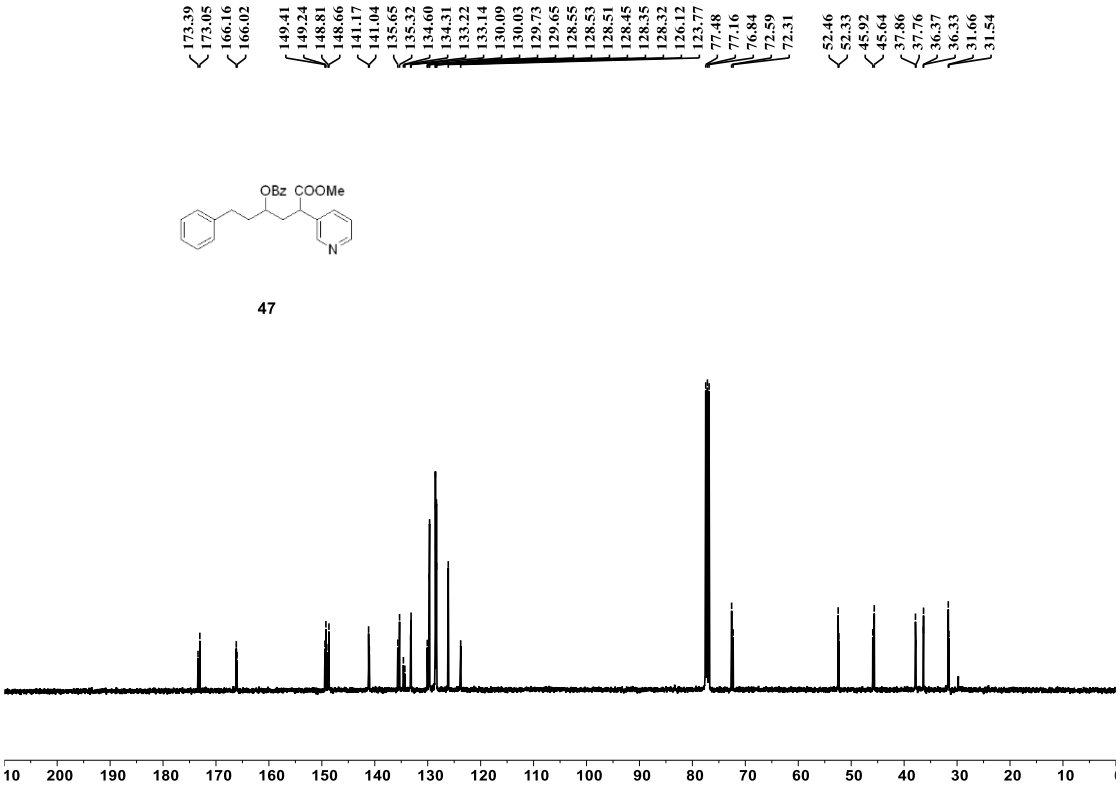


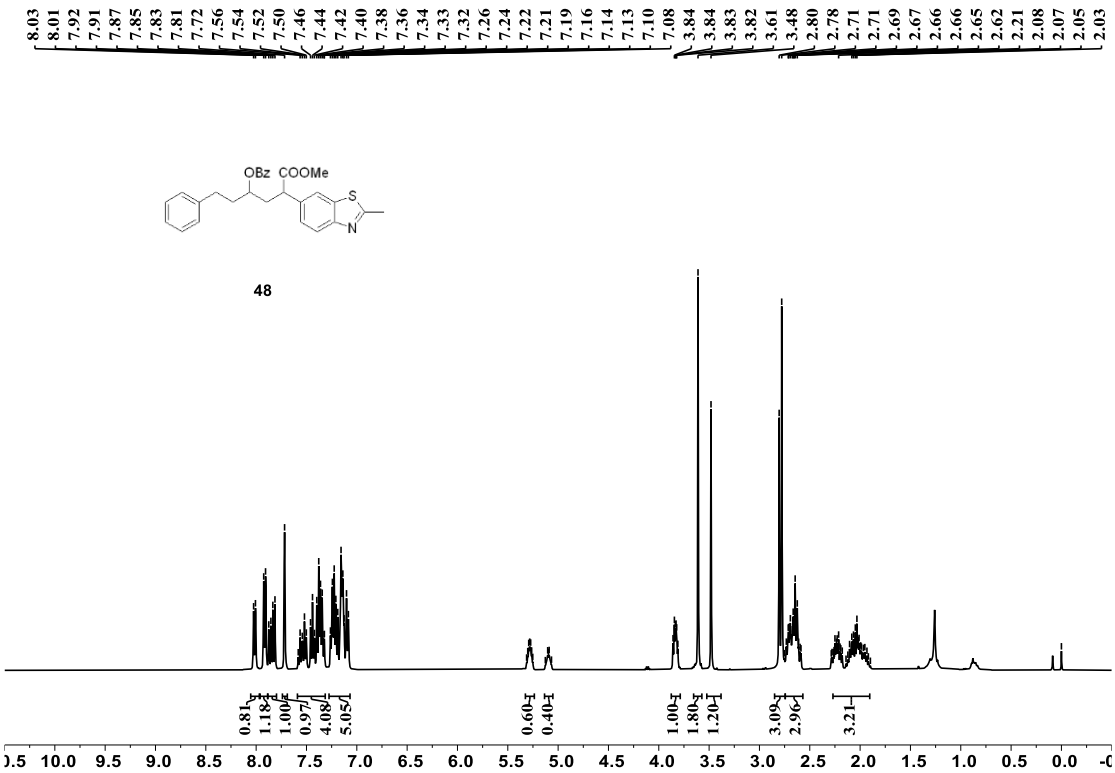
^{1}H NMR (500 MHz, $CDCl_3$)



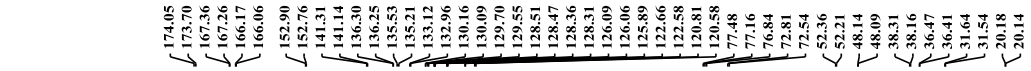
^{13}C NMR (101 MHz, $CDCl_3$)

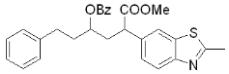


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)





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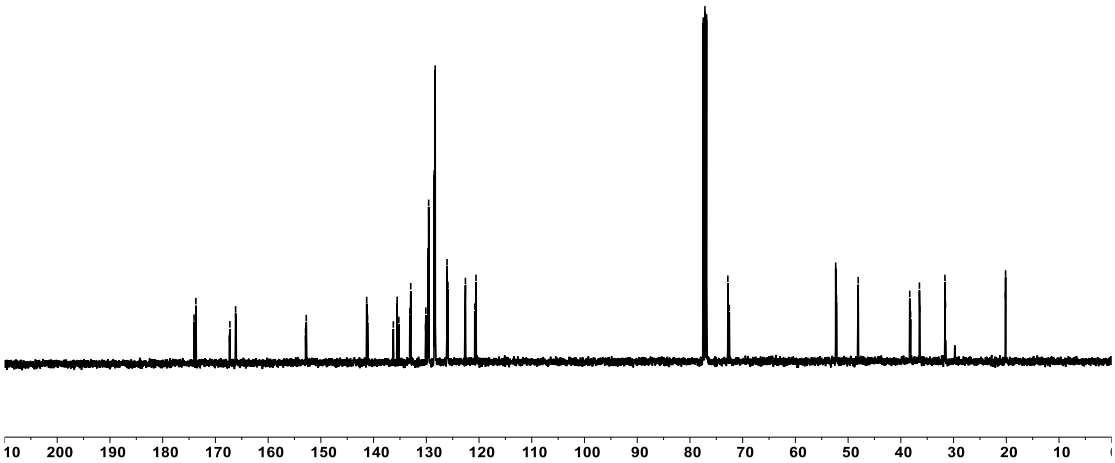
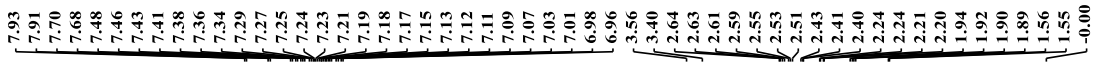
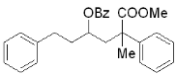


^{1}H NMR (400 MHz, $CDCl_3$)





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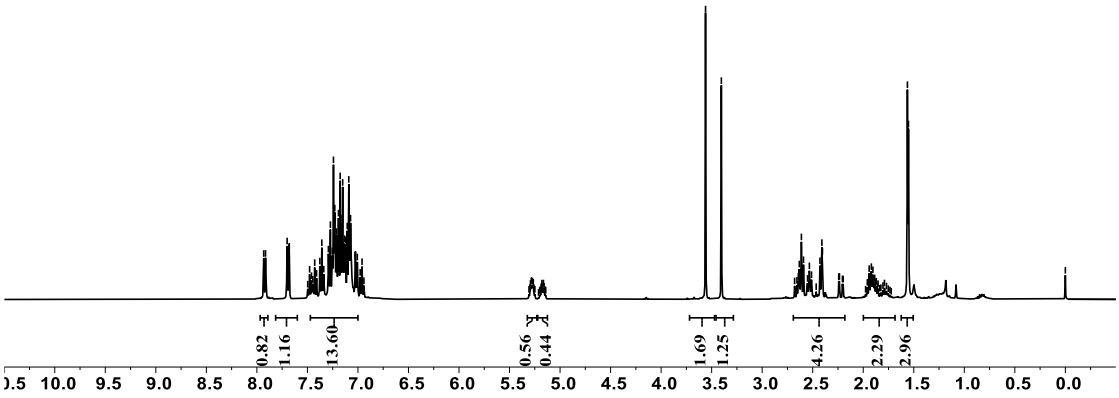
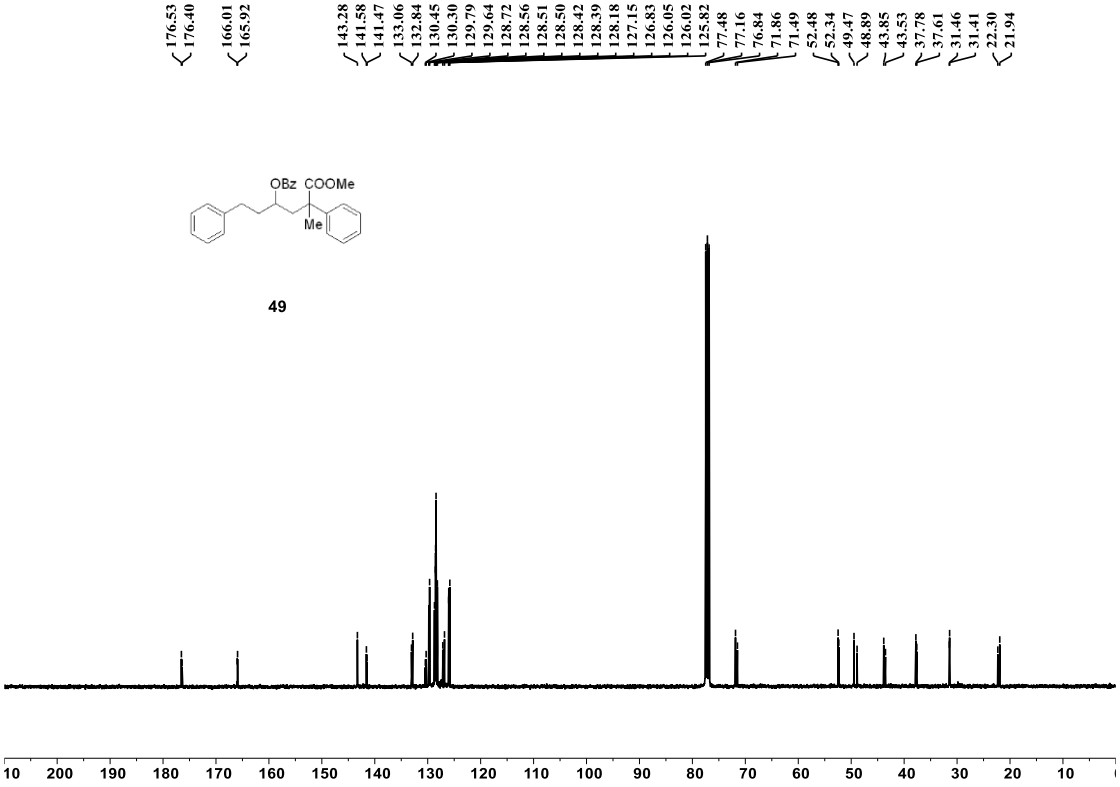
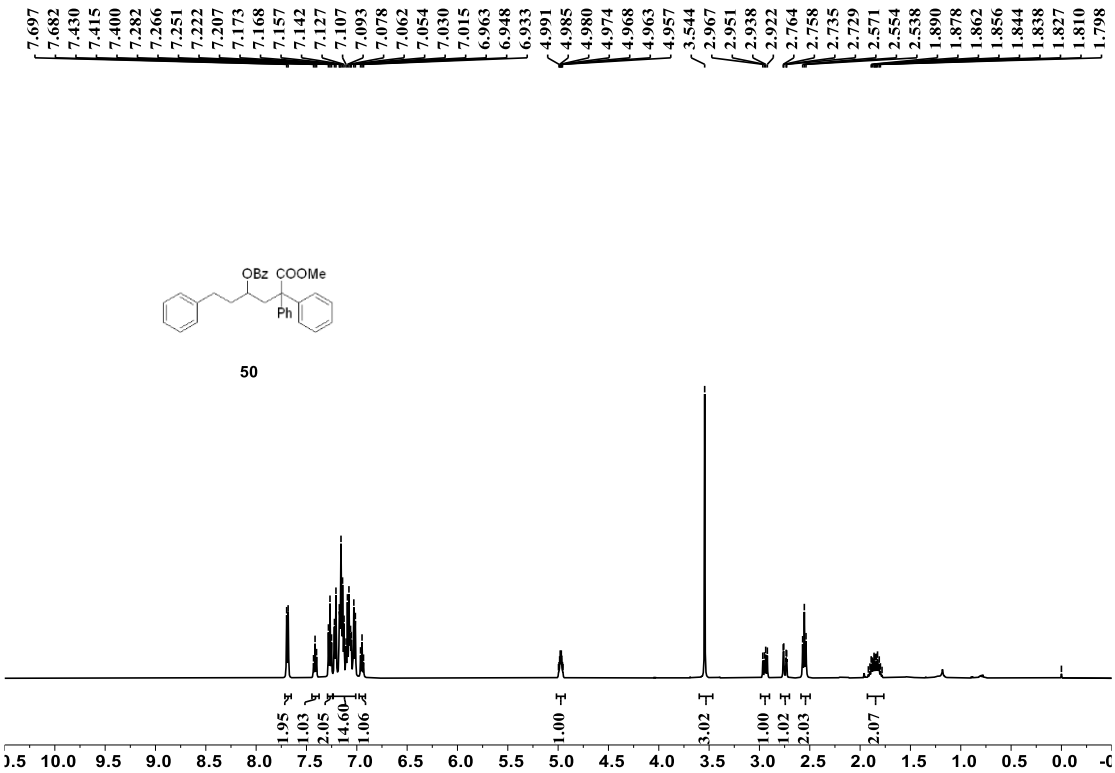


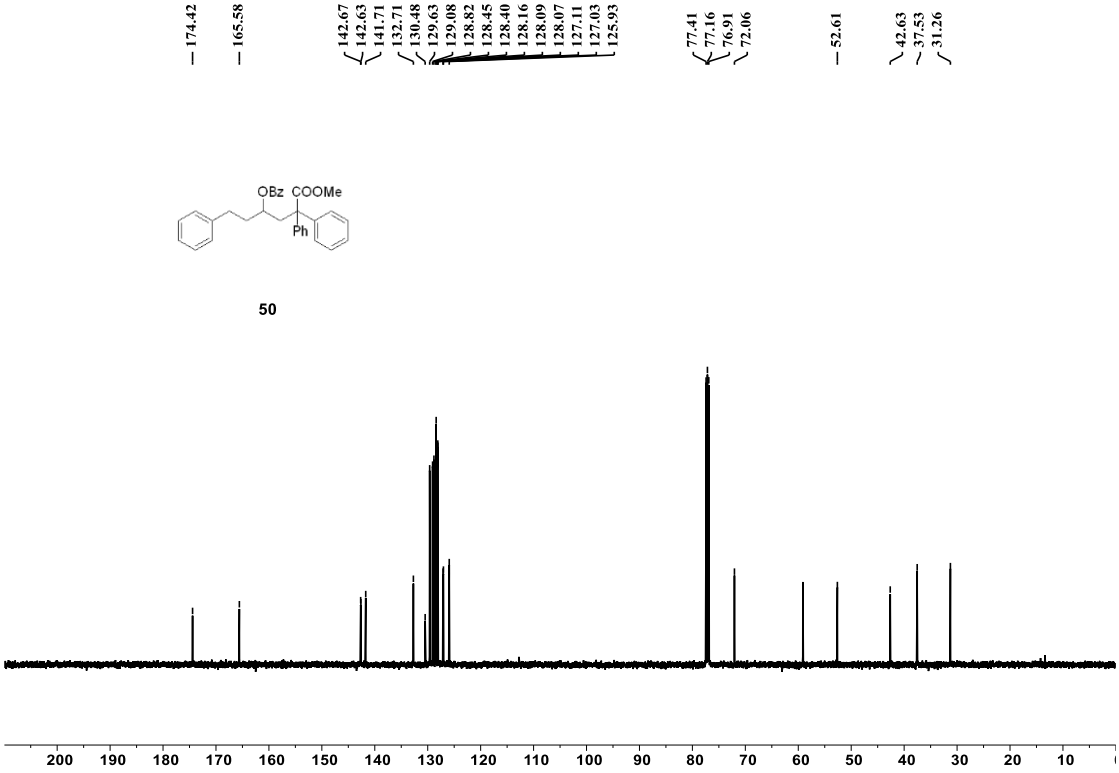
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

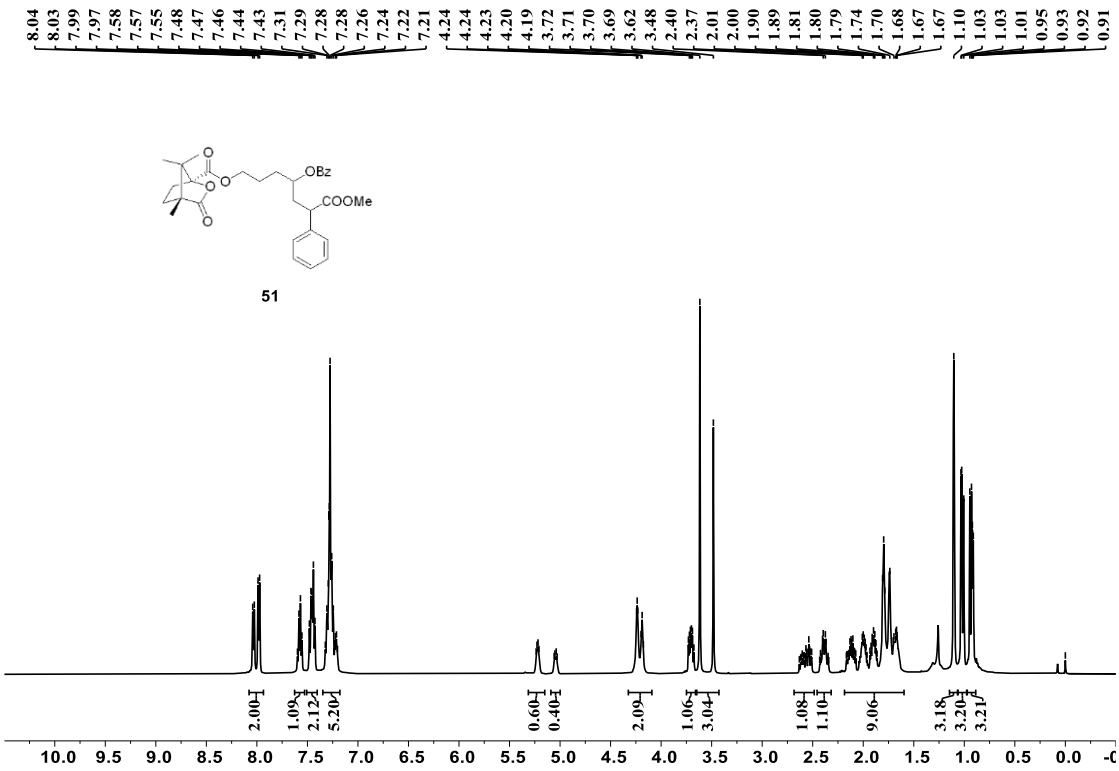


^{13}C NMR (101 MHz, $CDCl_3$)



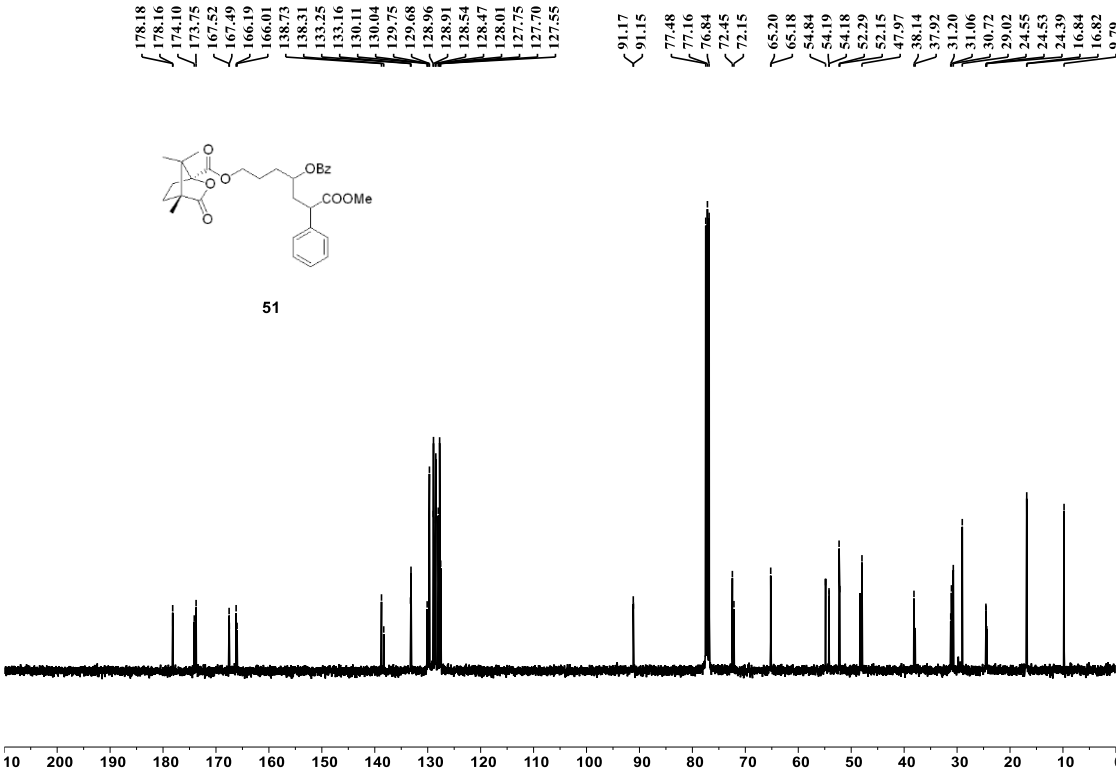
50

^{1}H NMR (500 MHz, $CDCl_3$)

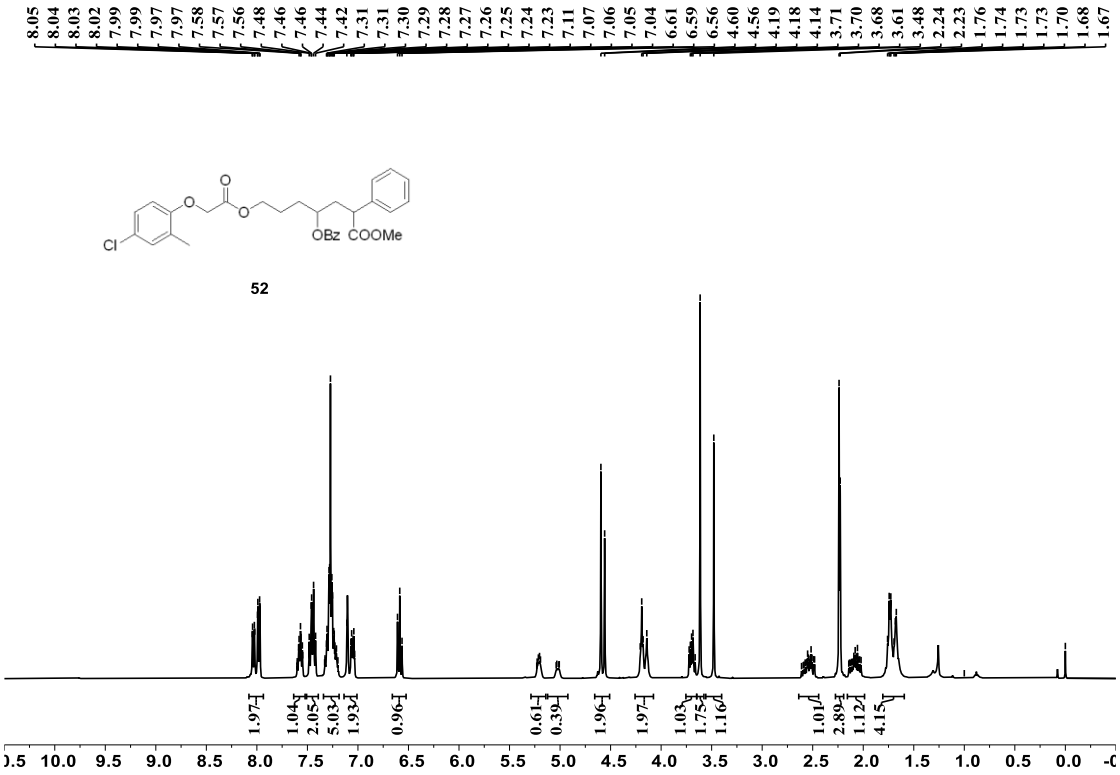


51

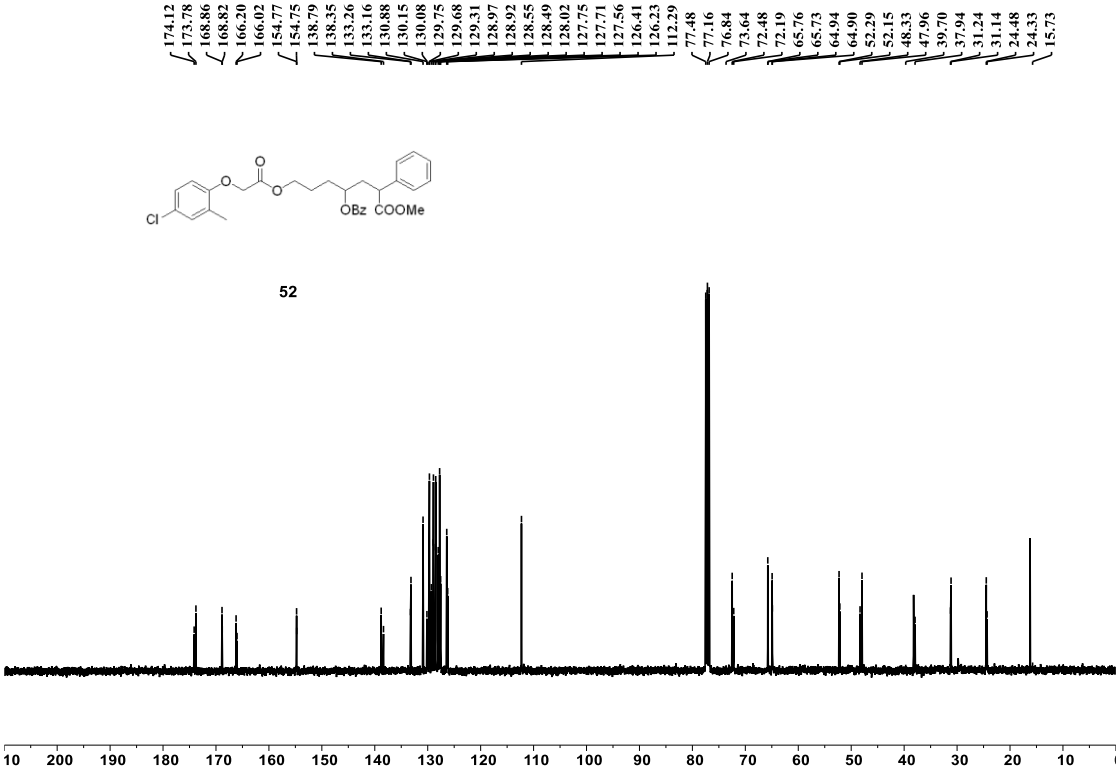
^{13}C NMR (101 MHz, $CDCl_3$)



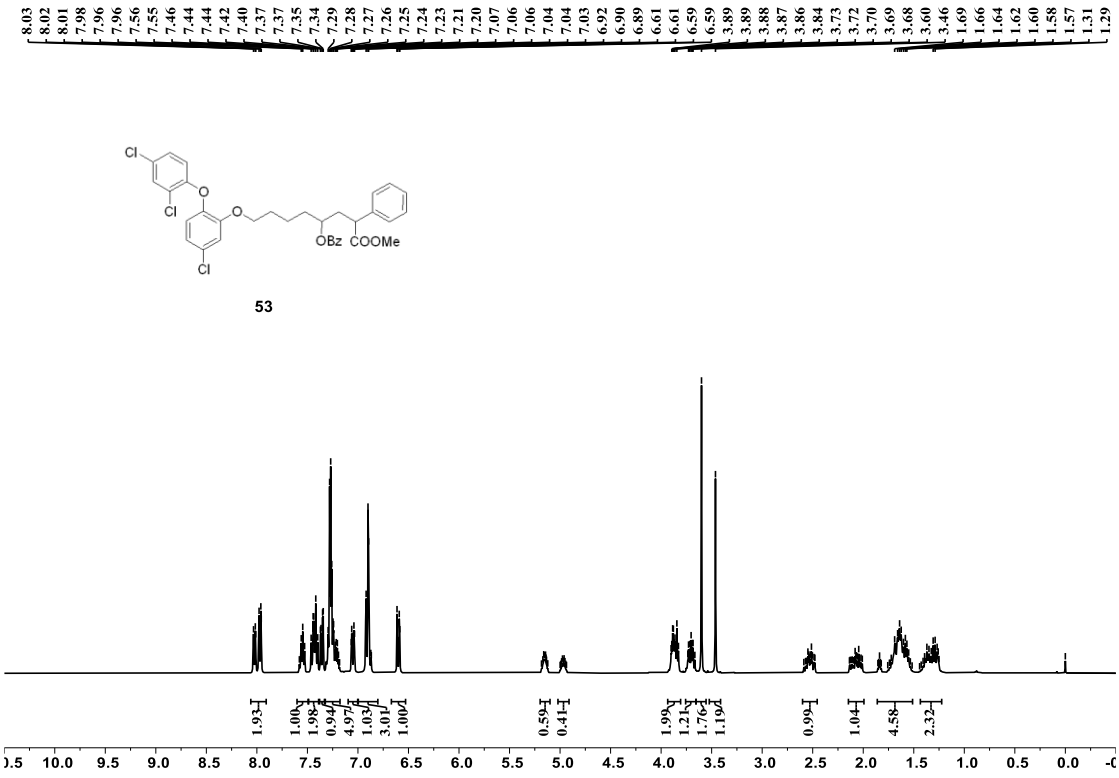
^{1}H NMR (400 MHz, $CDCl_3$)



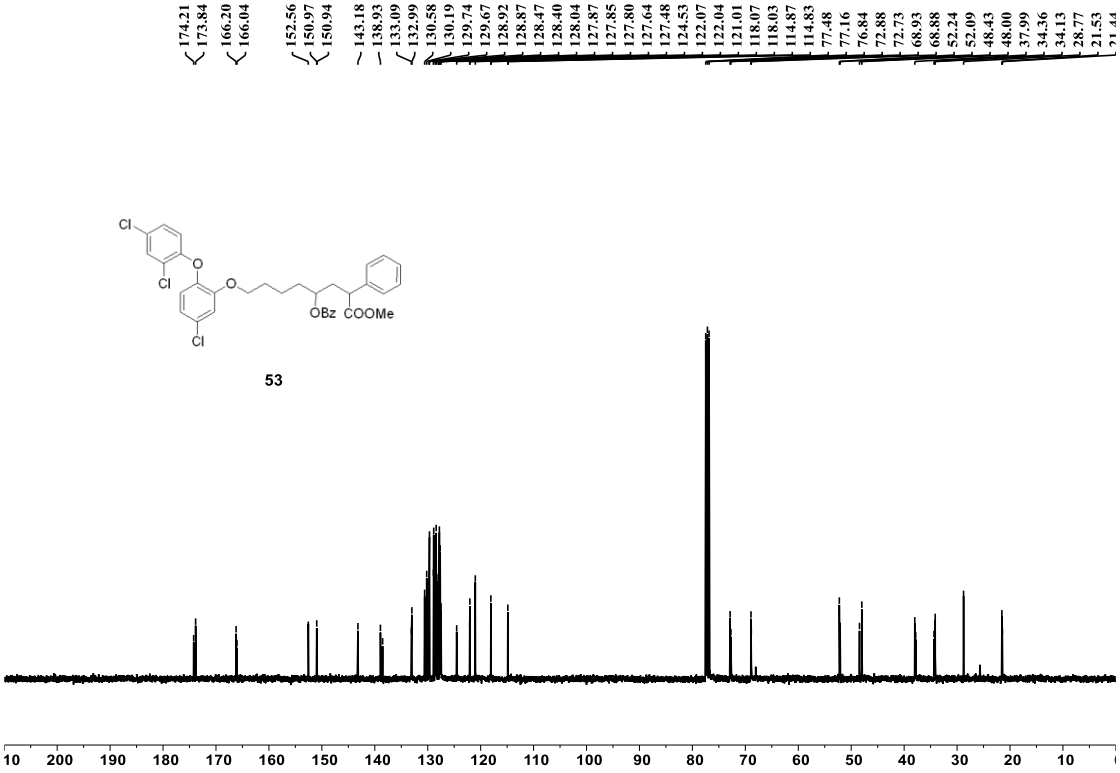
^{13}C NMR (101 MHz, $CDCl_3$)



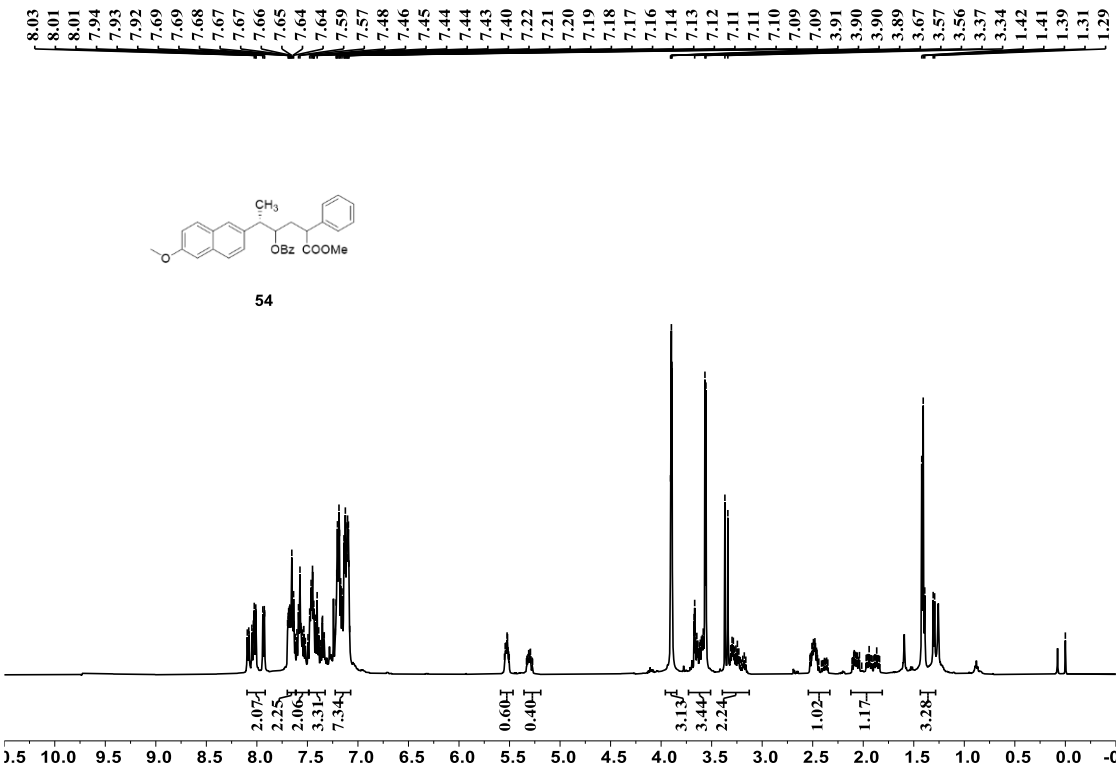
^{1}H NMR (400 MHz, $CDCl_3$)



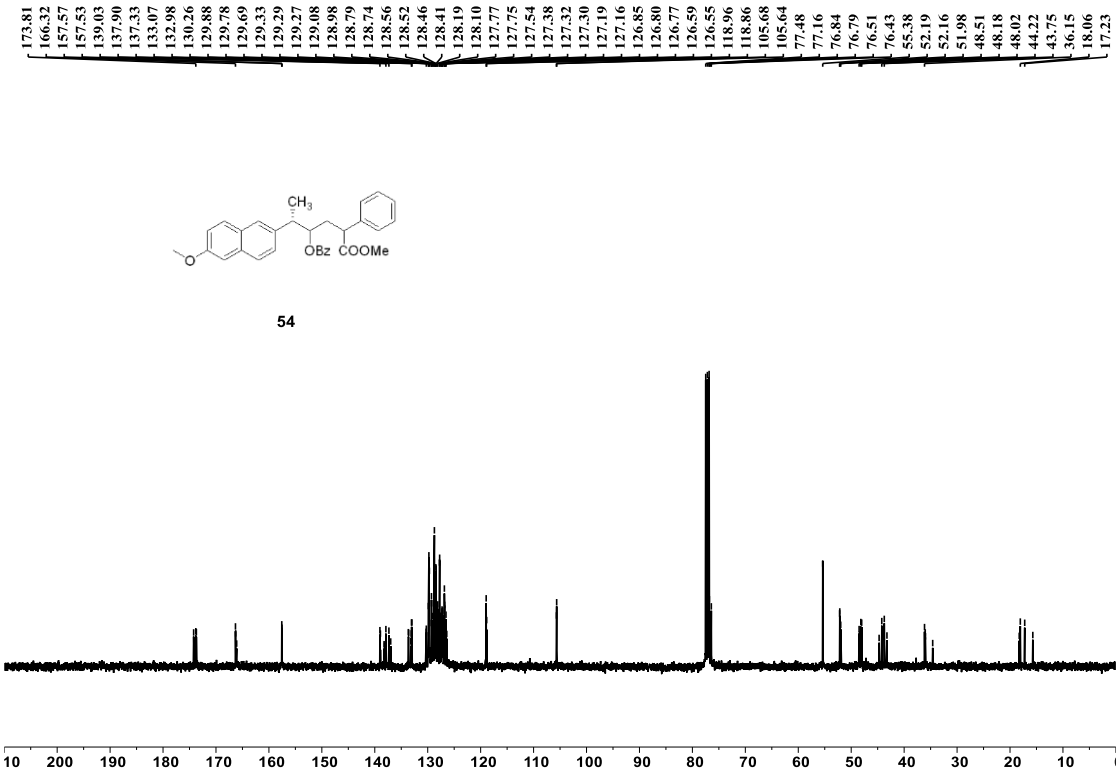
^{13}C NMR (101 MHz, $CDCl_3$)



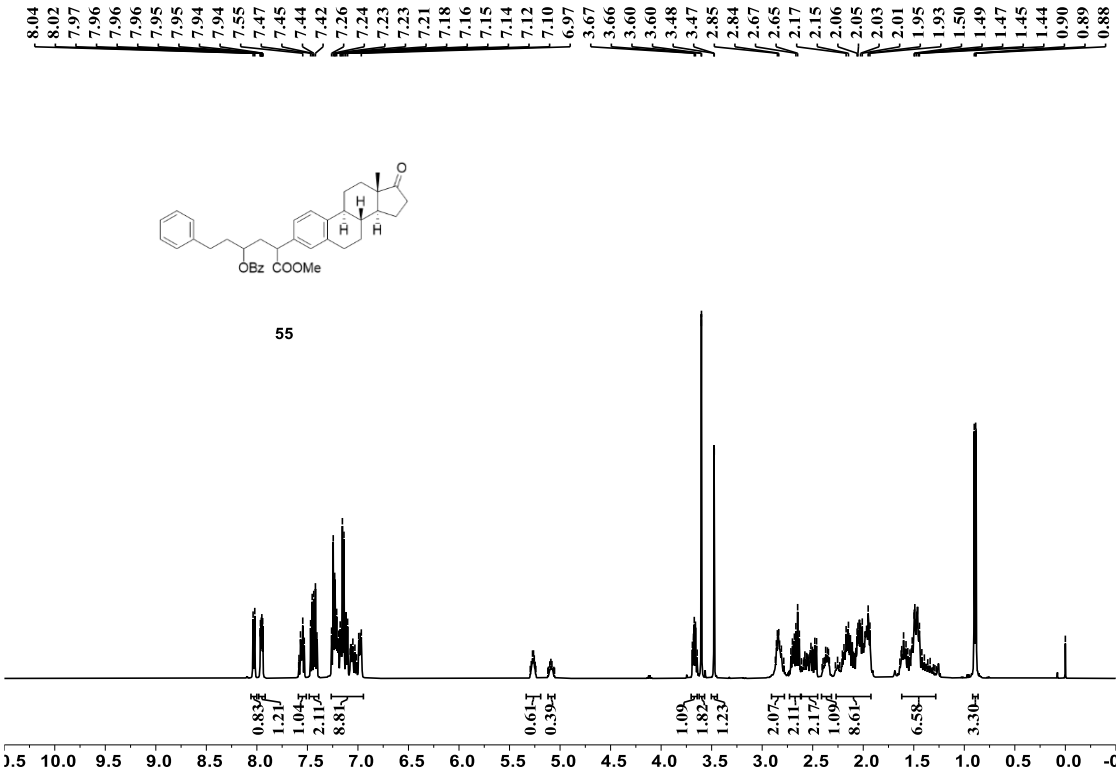
^{1}H NMR (500 MHz, $CDCl_3$)



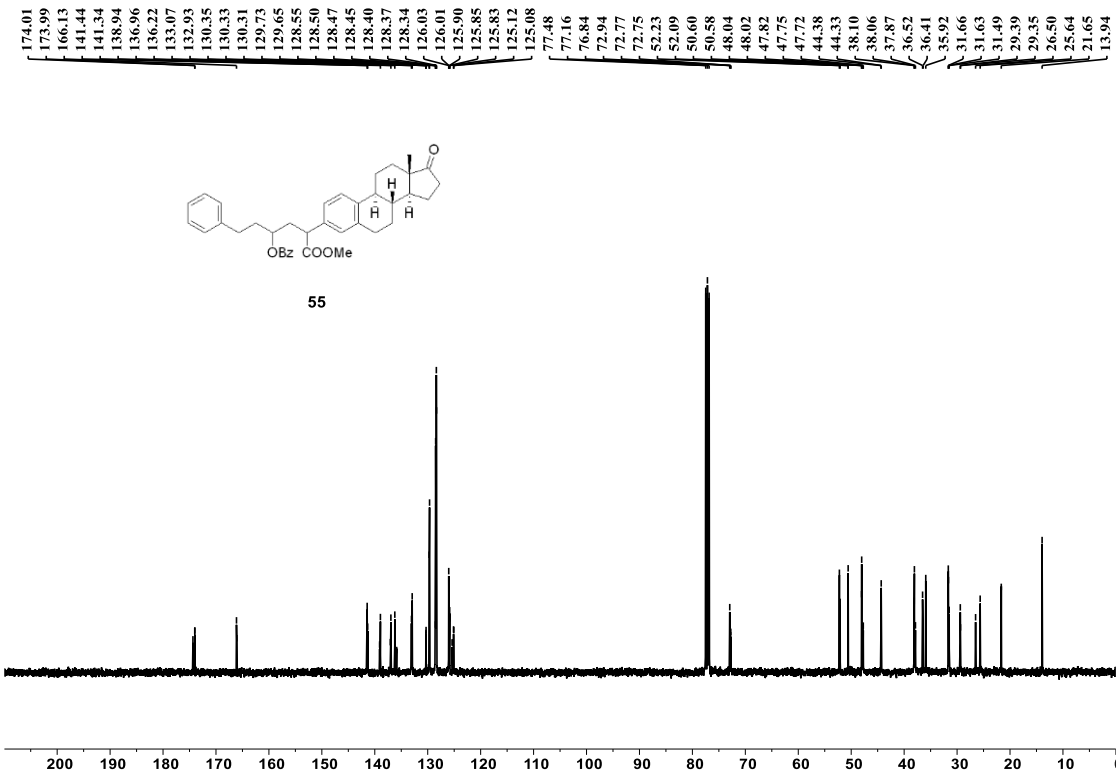
^{13}C NMR (101 MHz, $CDCl_3$)



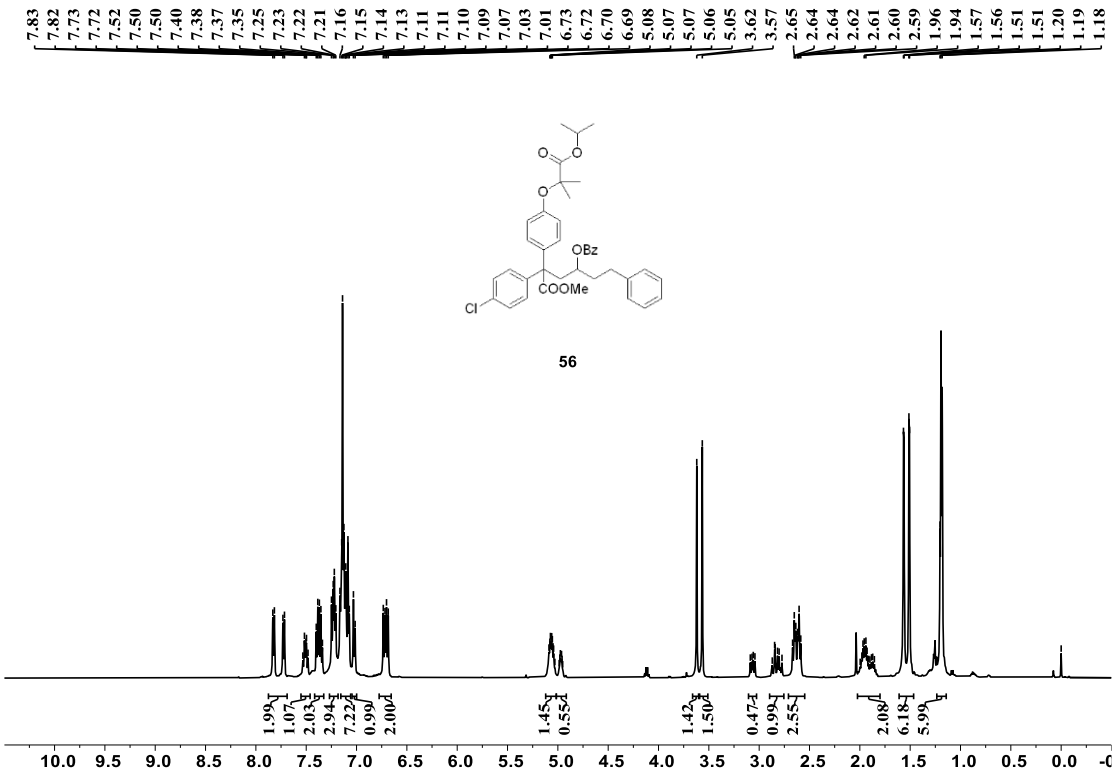
^{1}H NMR (500 MHz, $CDCl_3$)



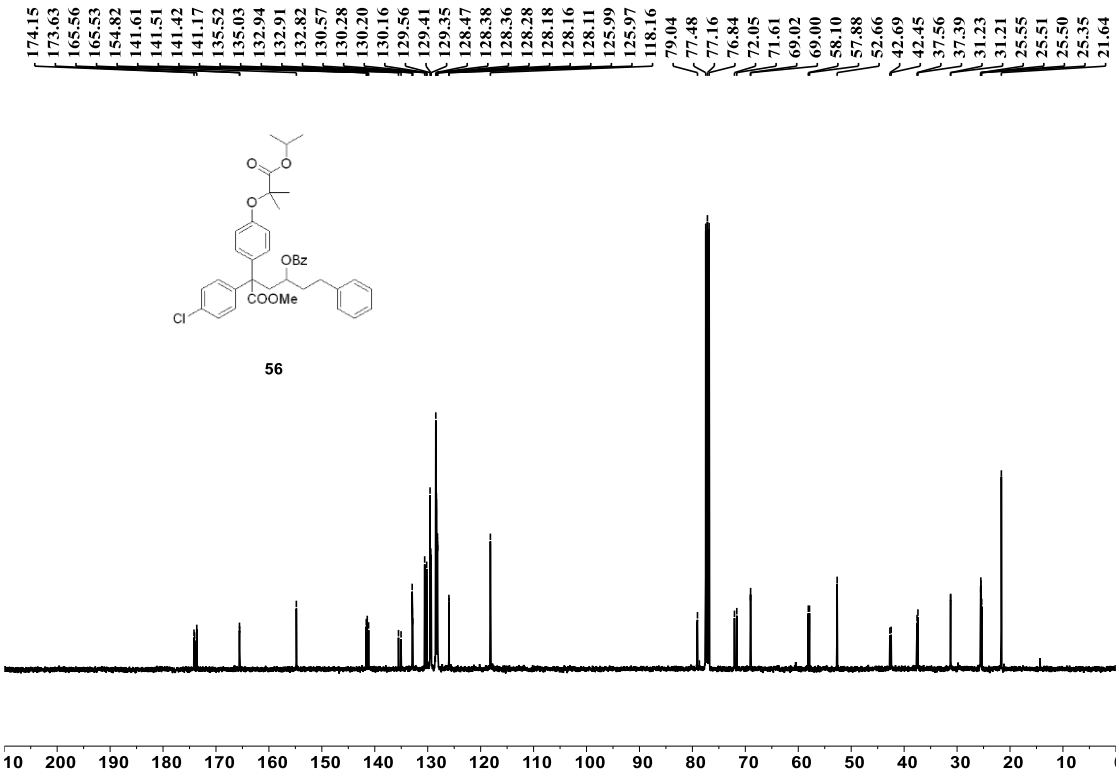
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

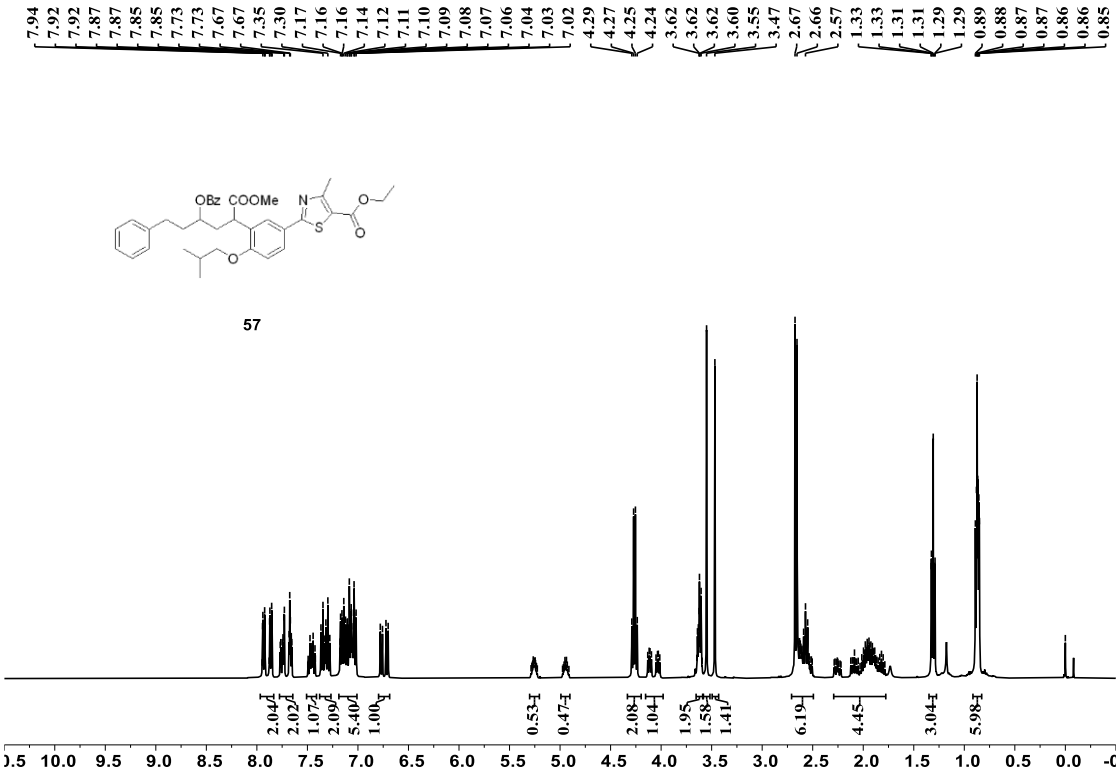


^{13}C NMR (101 MHz, $CDCl_3$)



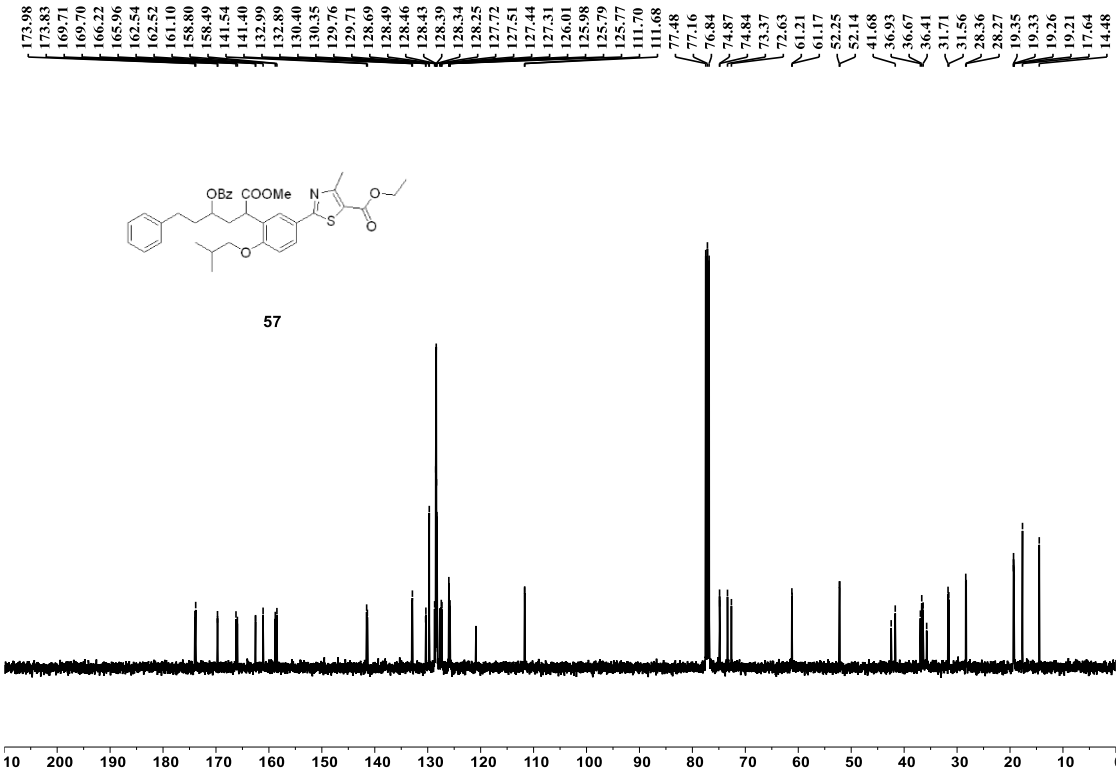
56

^{1}H NMR (400 MHz, $CDCl_3$)

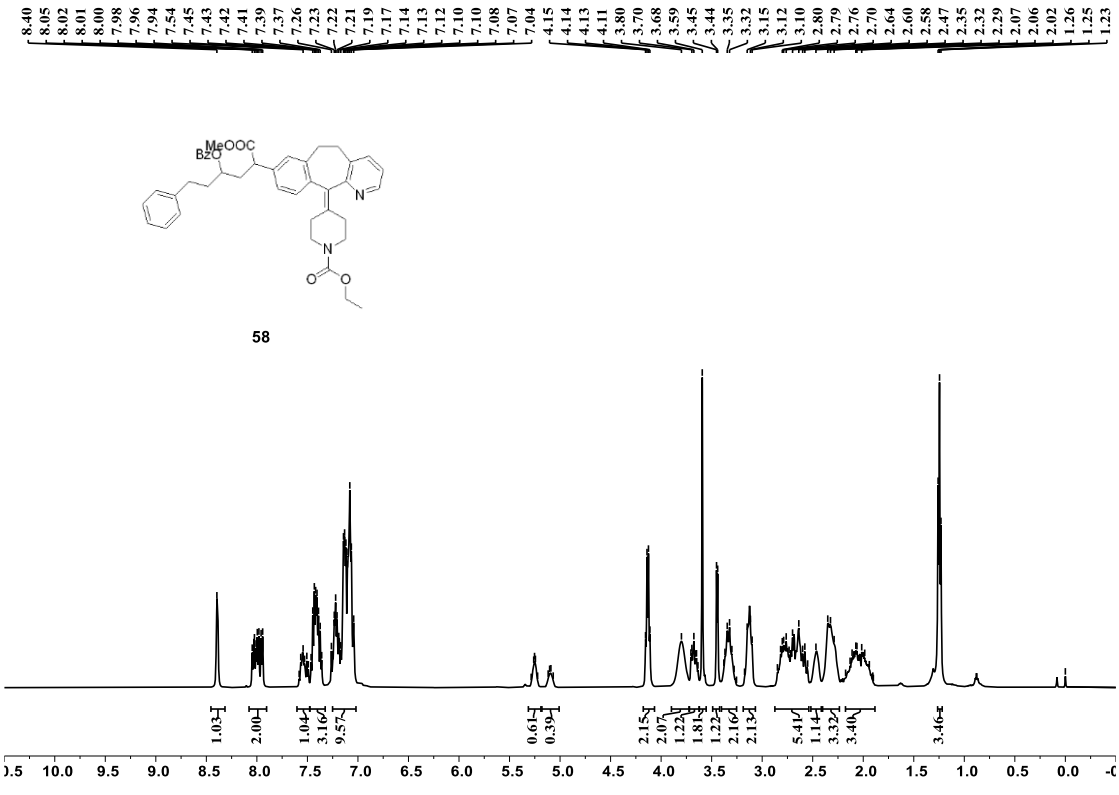


57

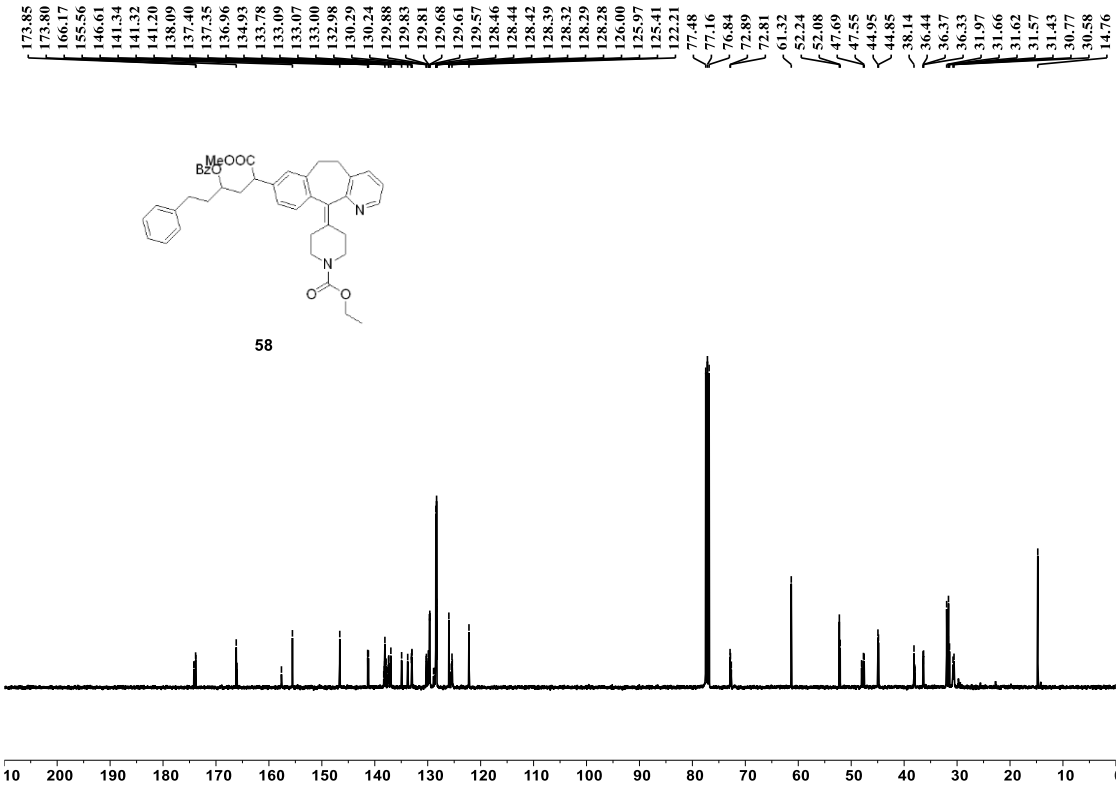
^{13}C NMR (101 MHz, $CDCl_3$)



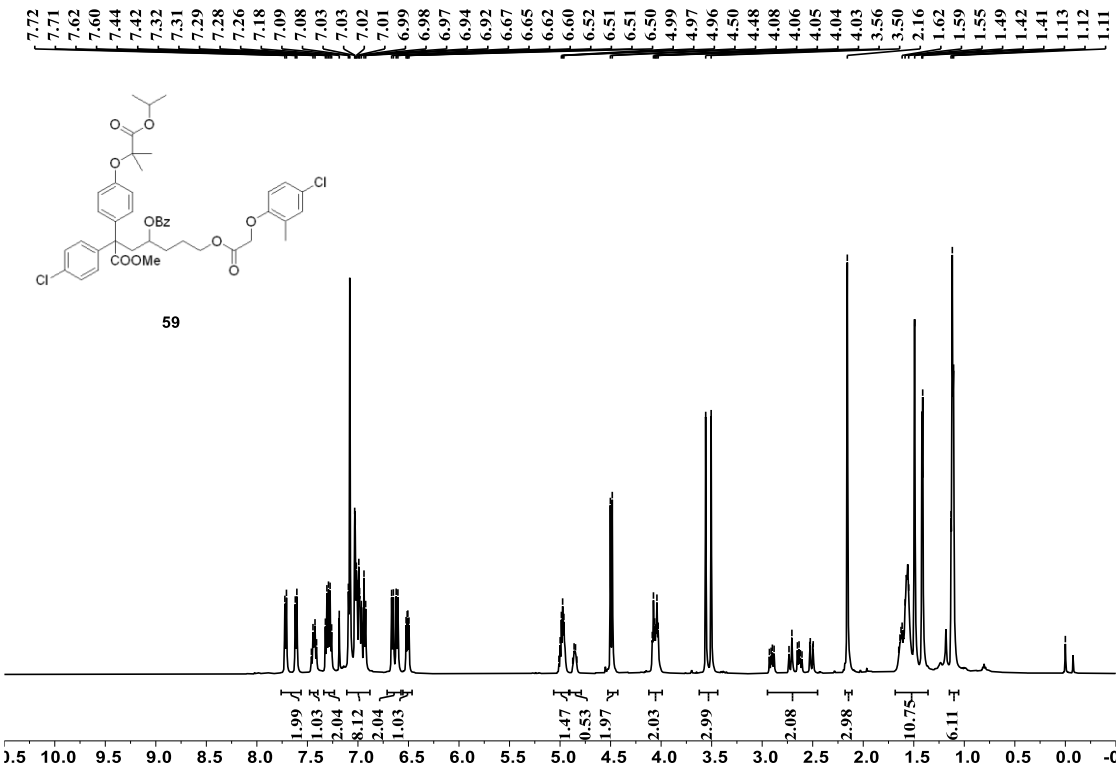
^{1}H NMR (500 MHz, $CDCl_3$)



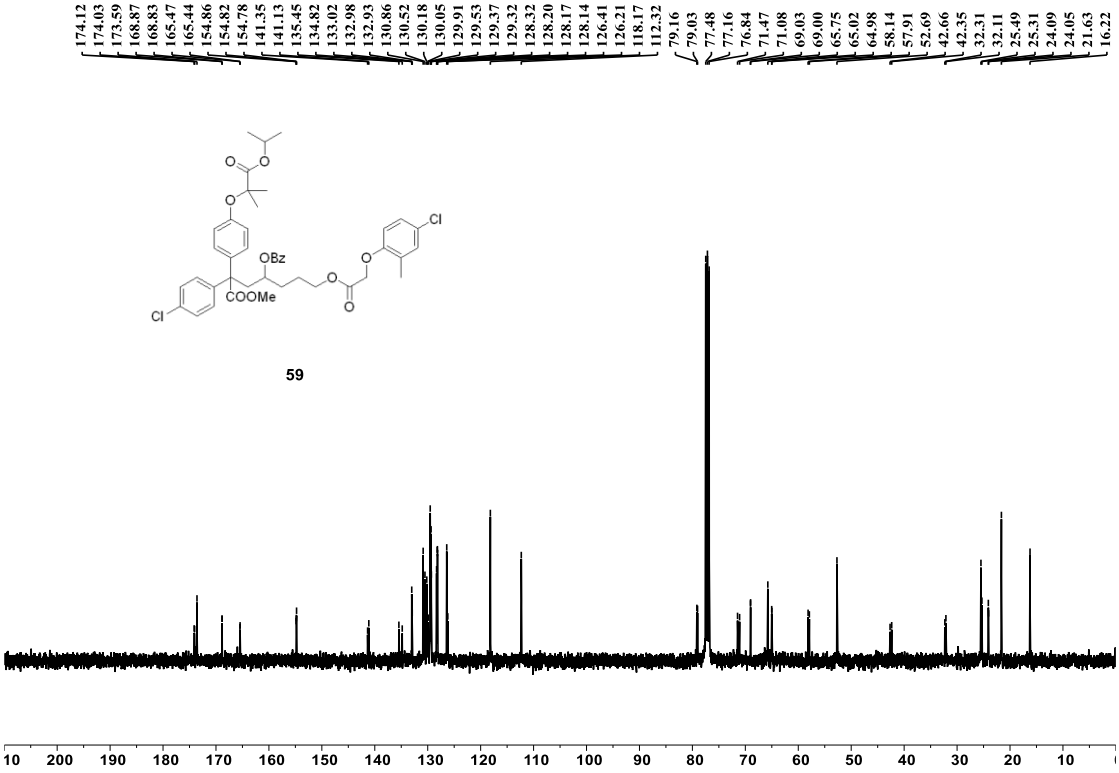
^{13}C NMR (101 MHz, $CDCl_3$)



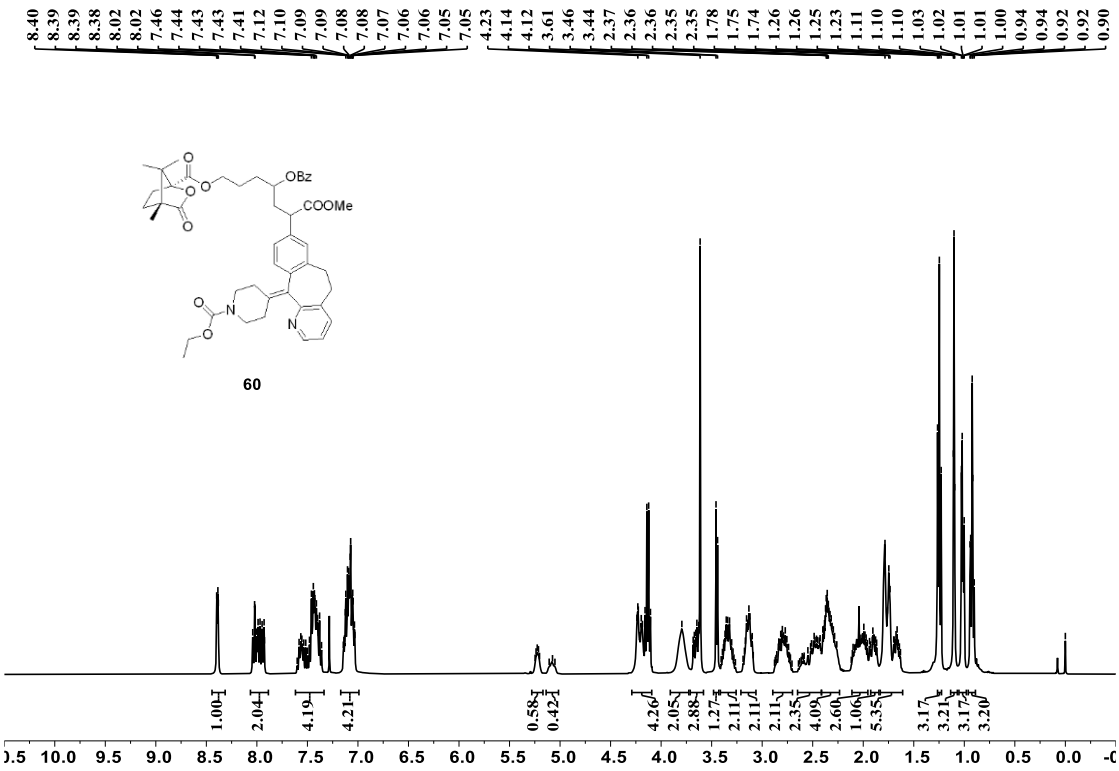
^{1}H NMR (500 MHz, $CDCl_3$)



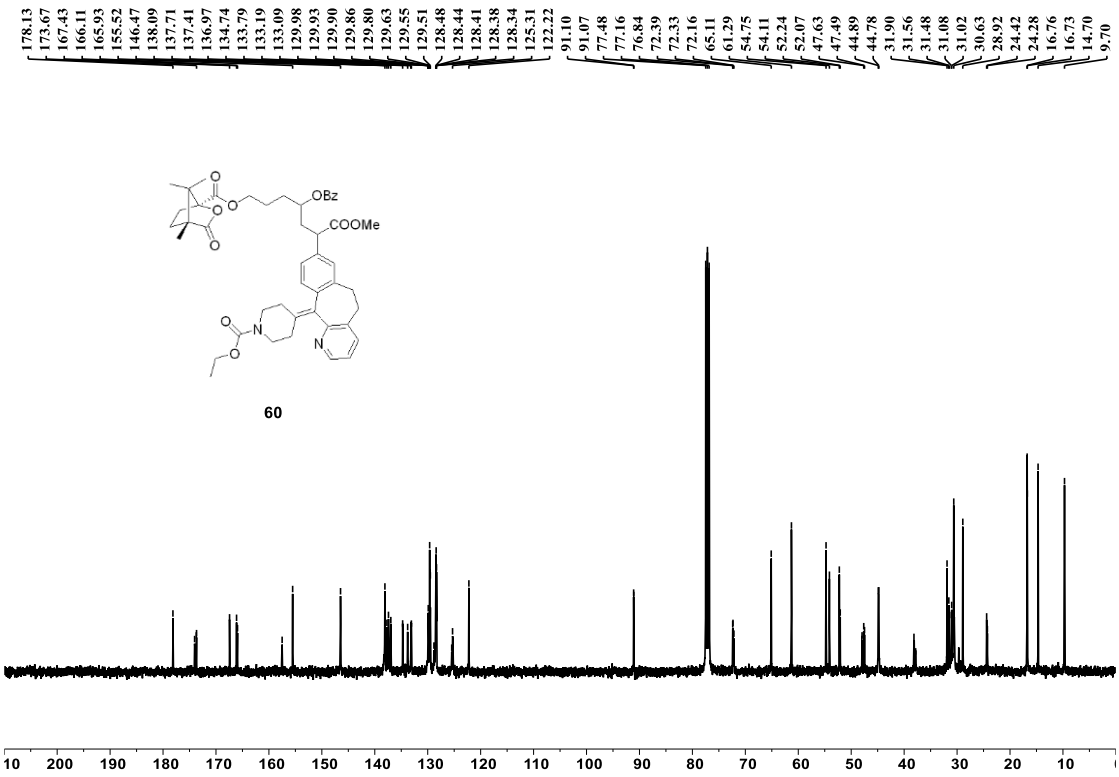
^{13}C NMR (101 MHz, $CDCl_3$)



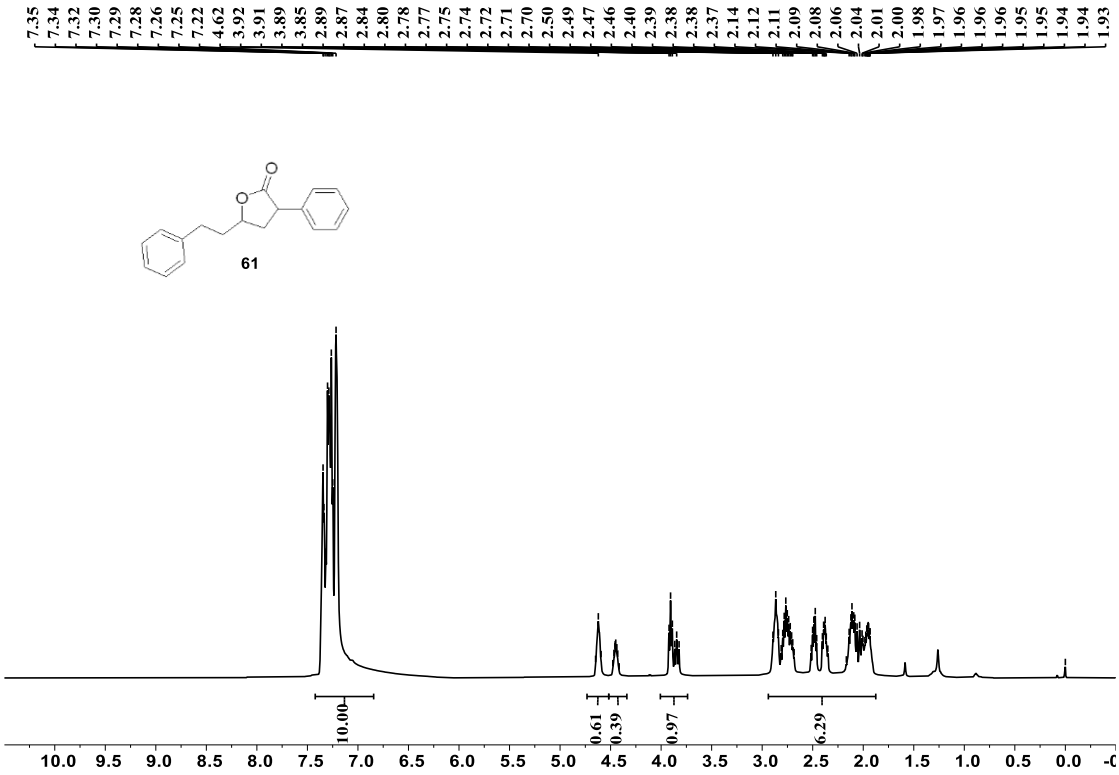
^{1}H NMR (400 MHz, $CDCl_3$)



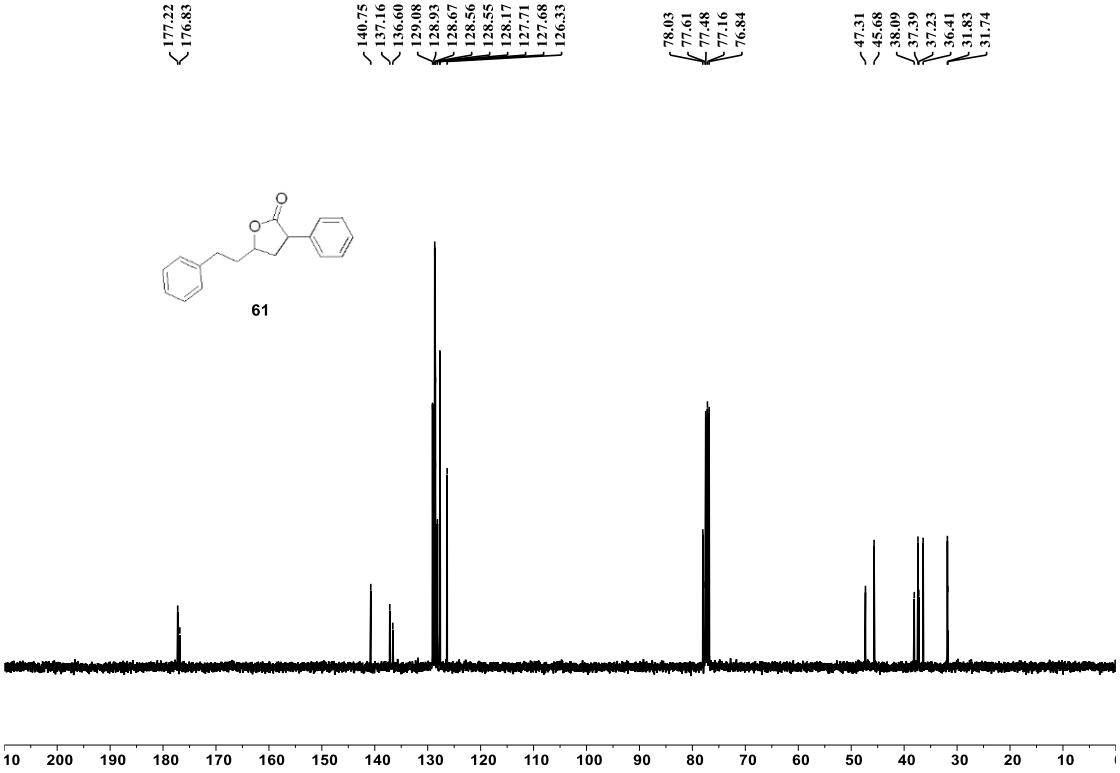
^{13}C NMR (101 MHz, $CDCl_3$)



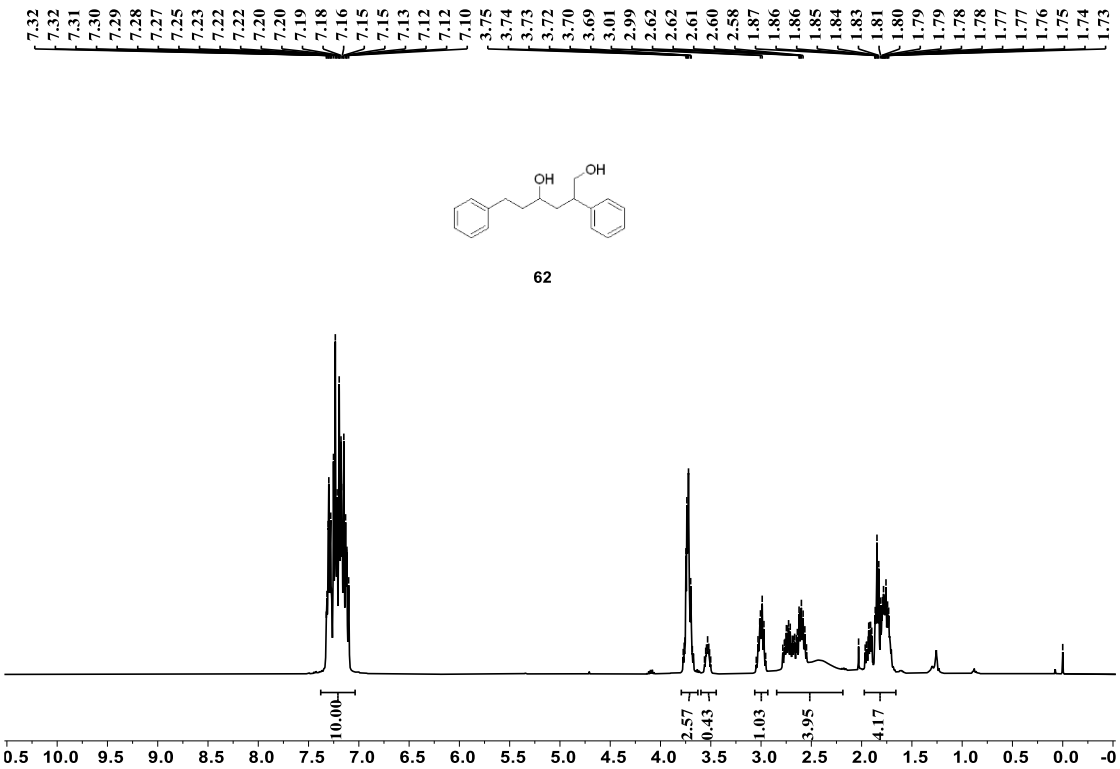
^{1}H NMR (500 MHz, $CDCl_3$)



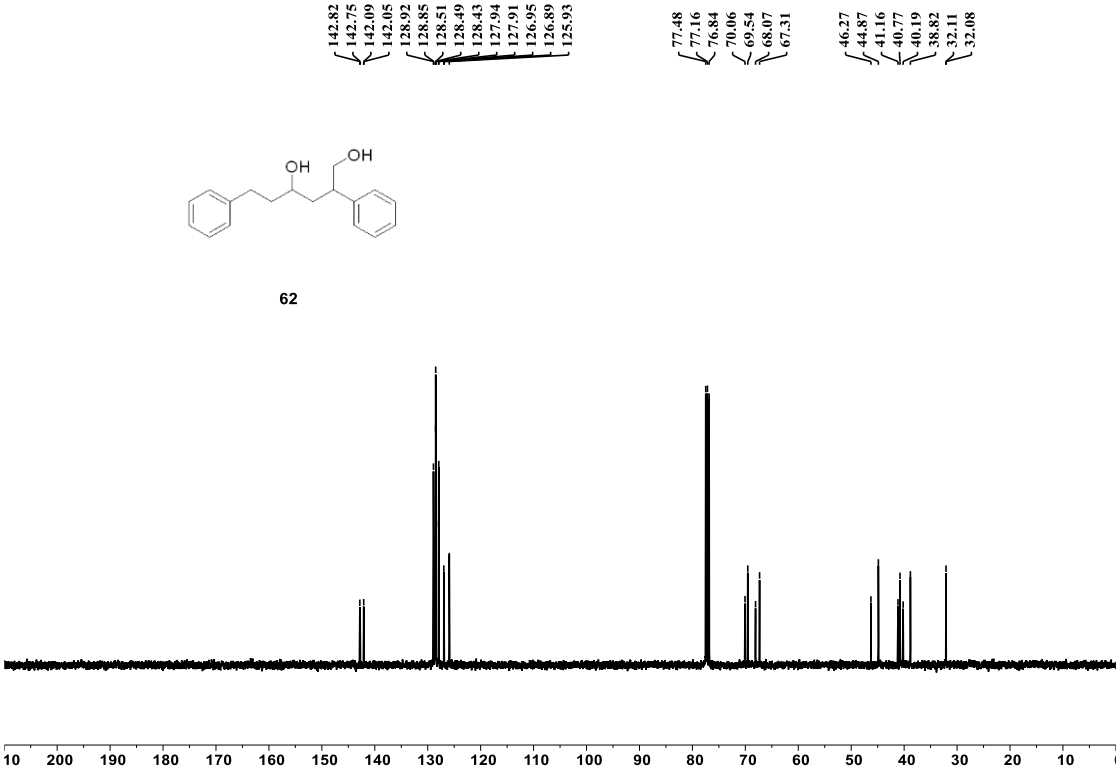
^{13}C NMR (101 MHz, $CDCl_3$)



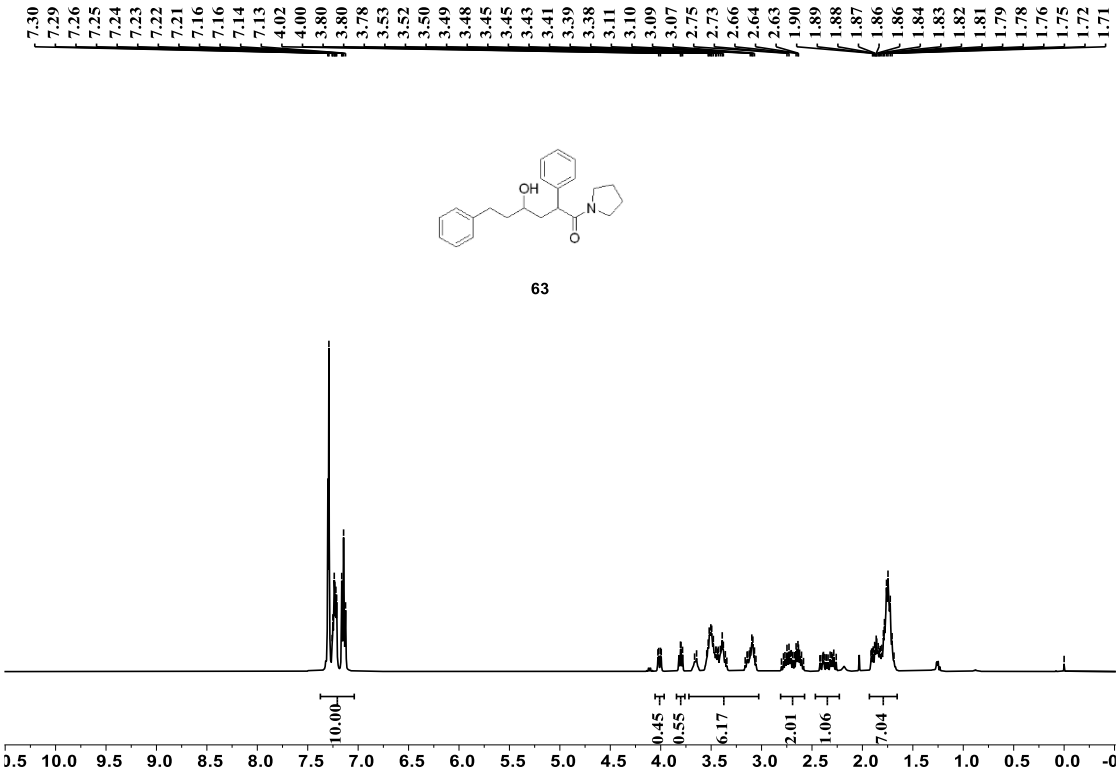
^{1}H NMR (400 MHz, $CDCl_3$)



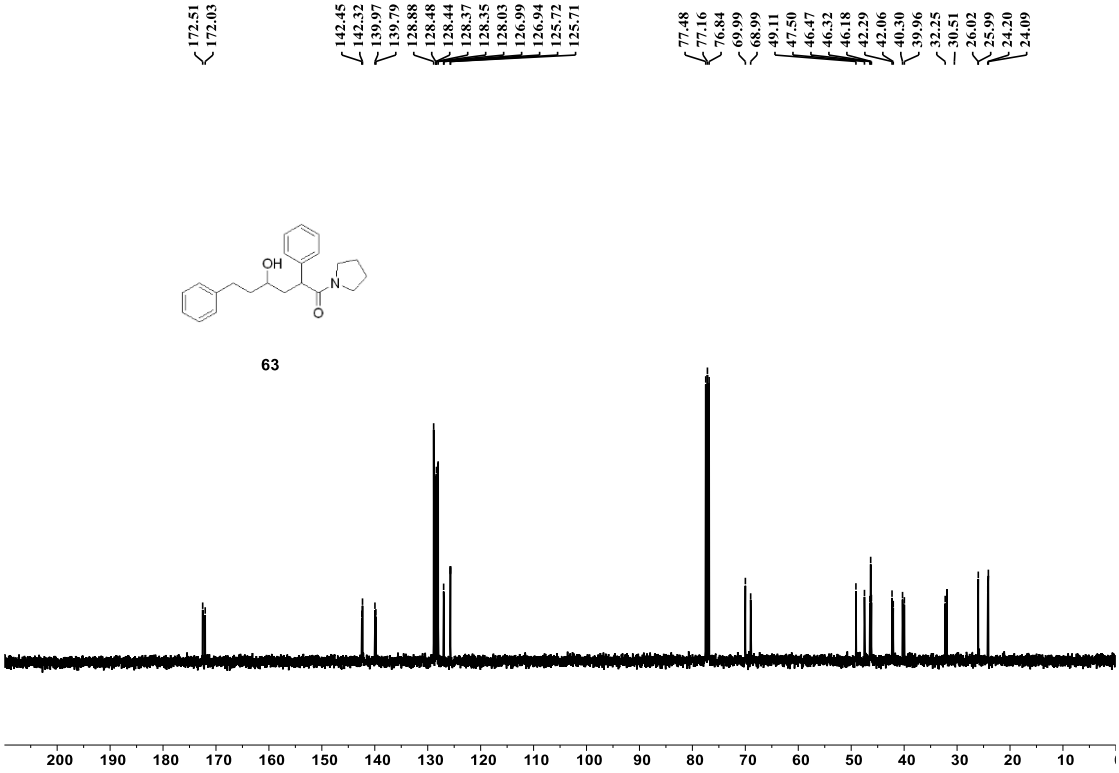
^{13}C NMR (101 MHz, $CDCl_3$)



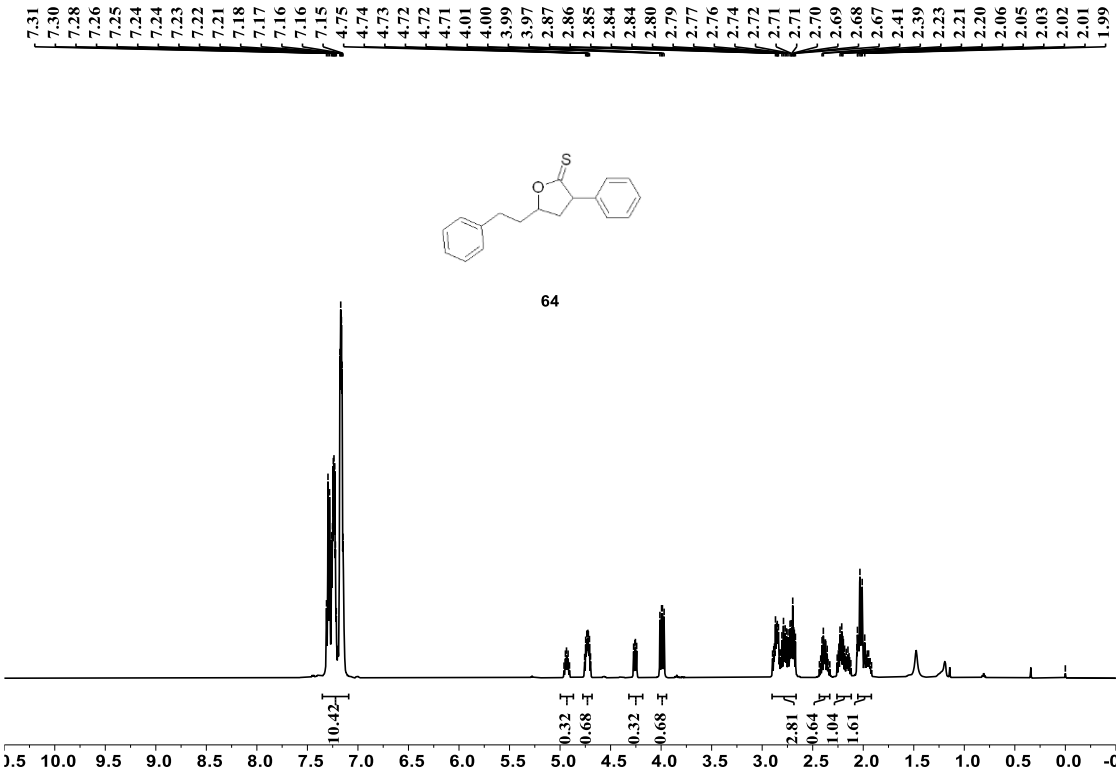
H NMR (400 MHz, $CDCl_3$)



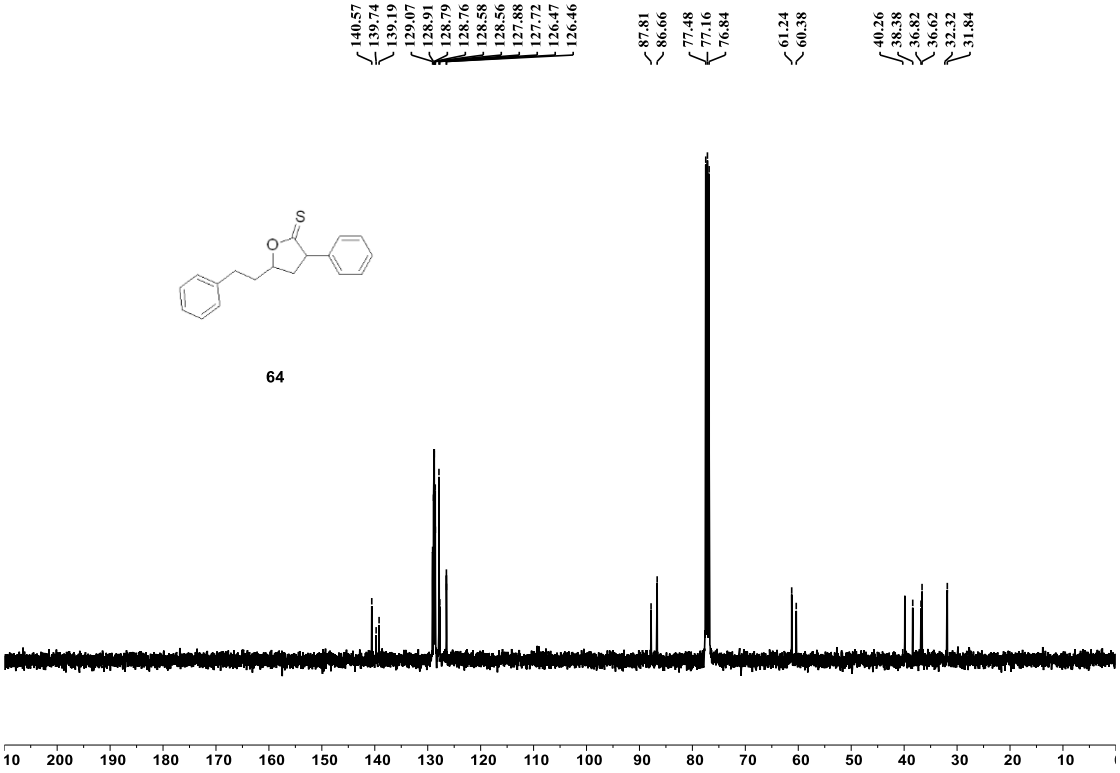
^{13}C NMR (101 MHz, $CDCl_3$)



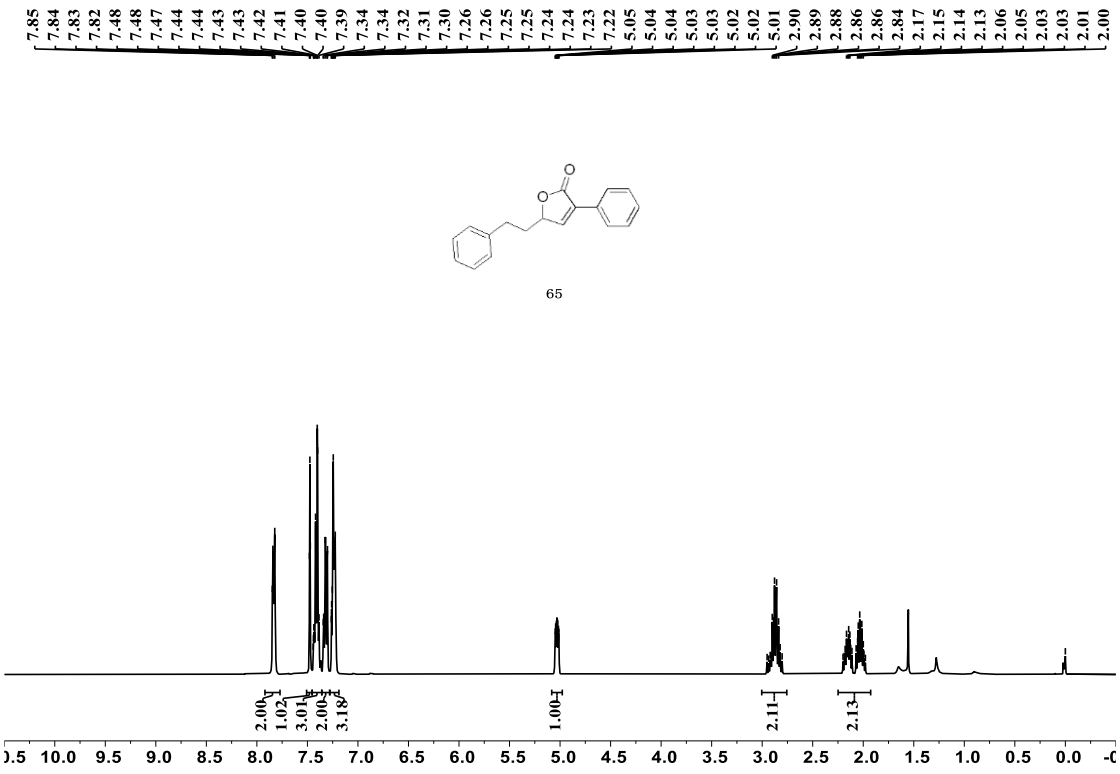
^{1}H NMR (500 MHz, $CDCl_3$)



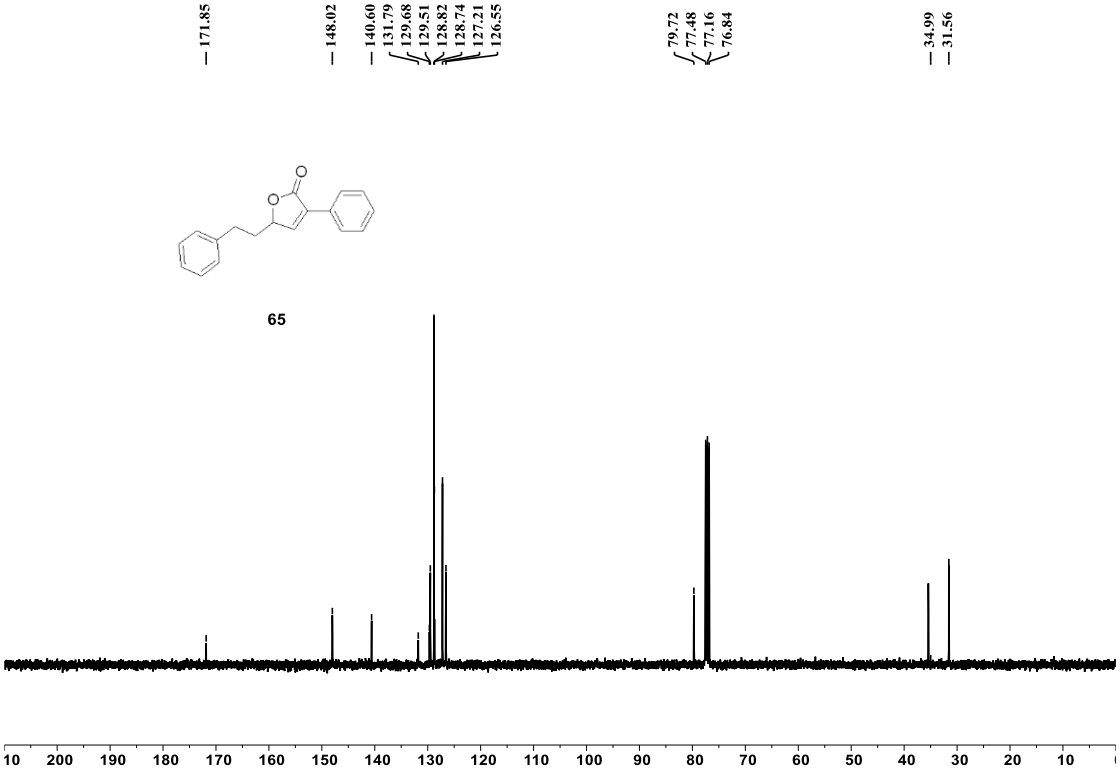
^{13}C NMR (101 MHz, $CDCl_3$)



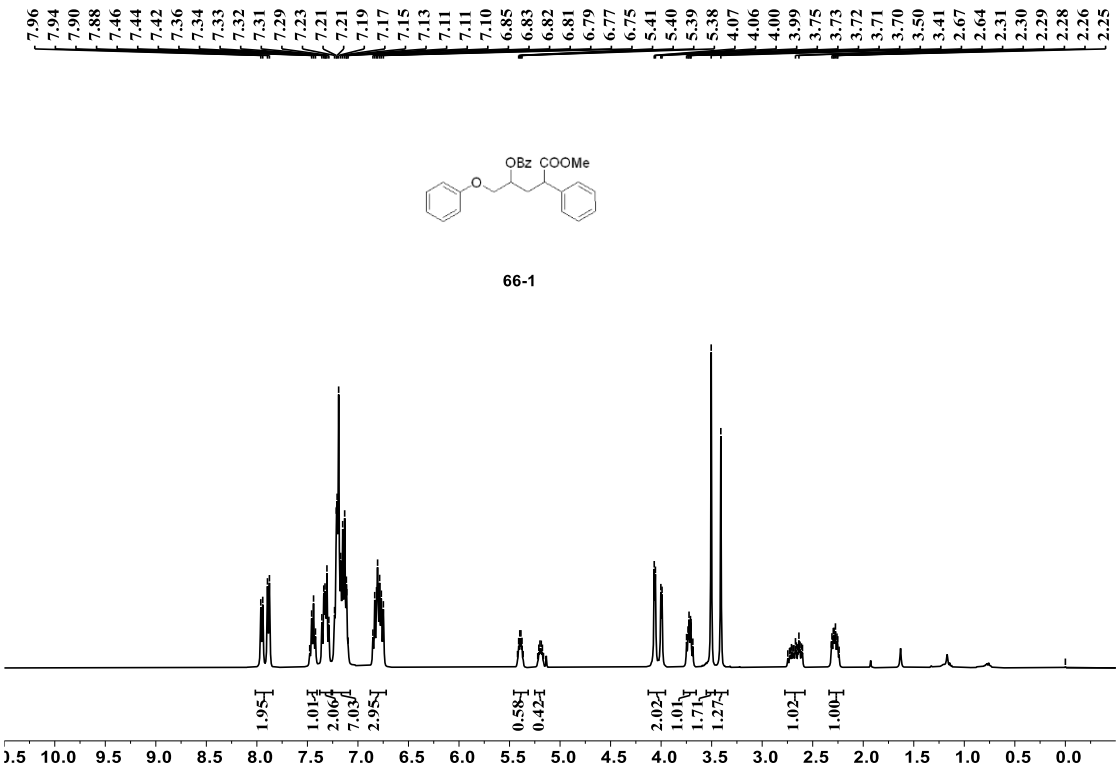
^{1}H NMR (400 MHz, $CDCl_3$)



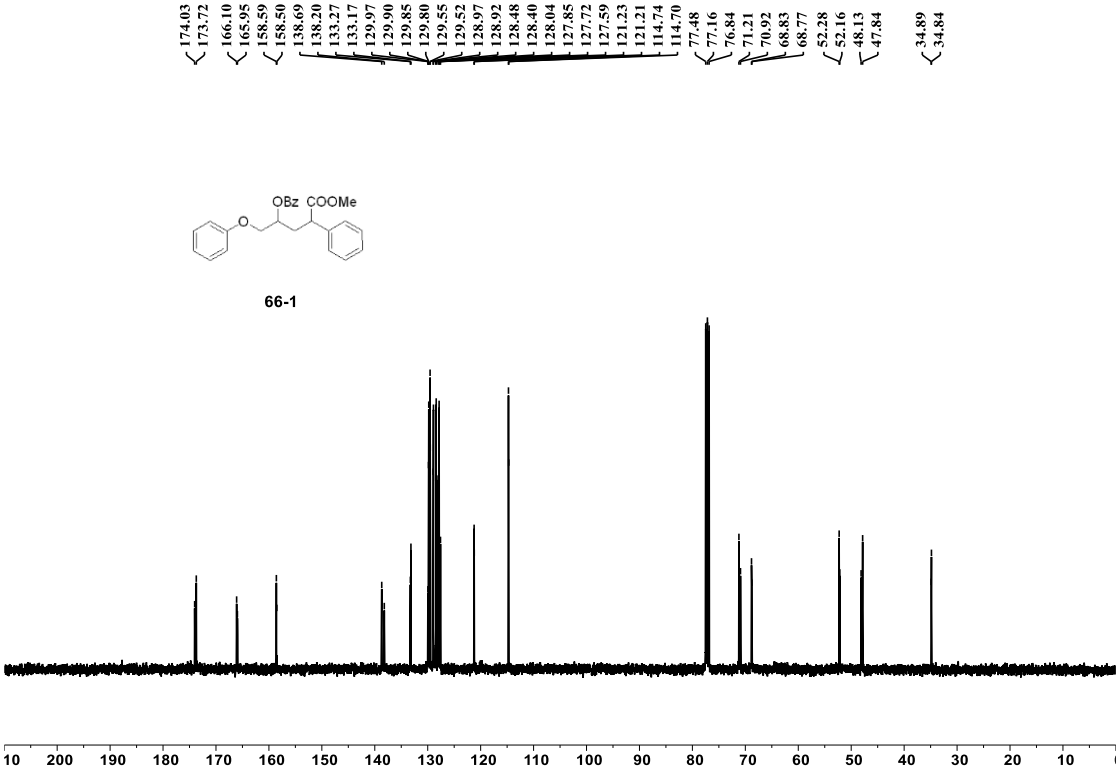
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



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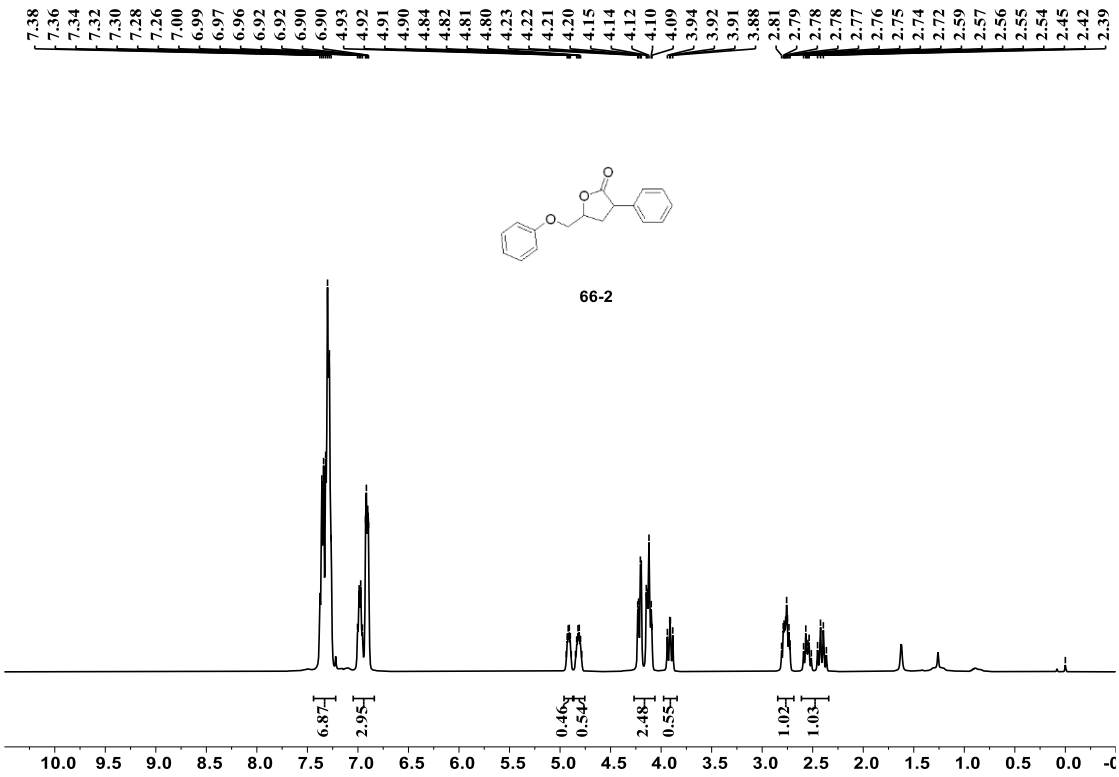

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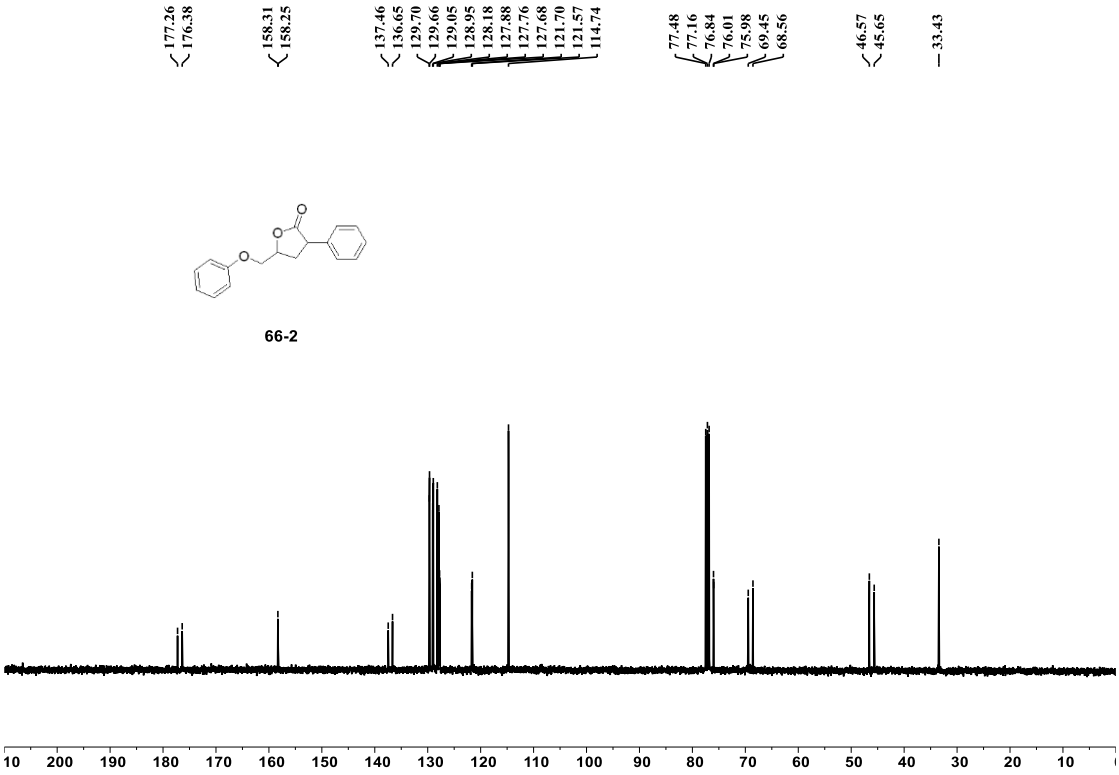

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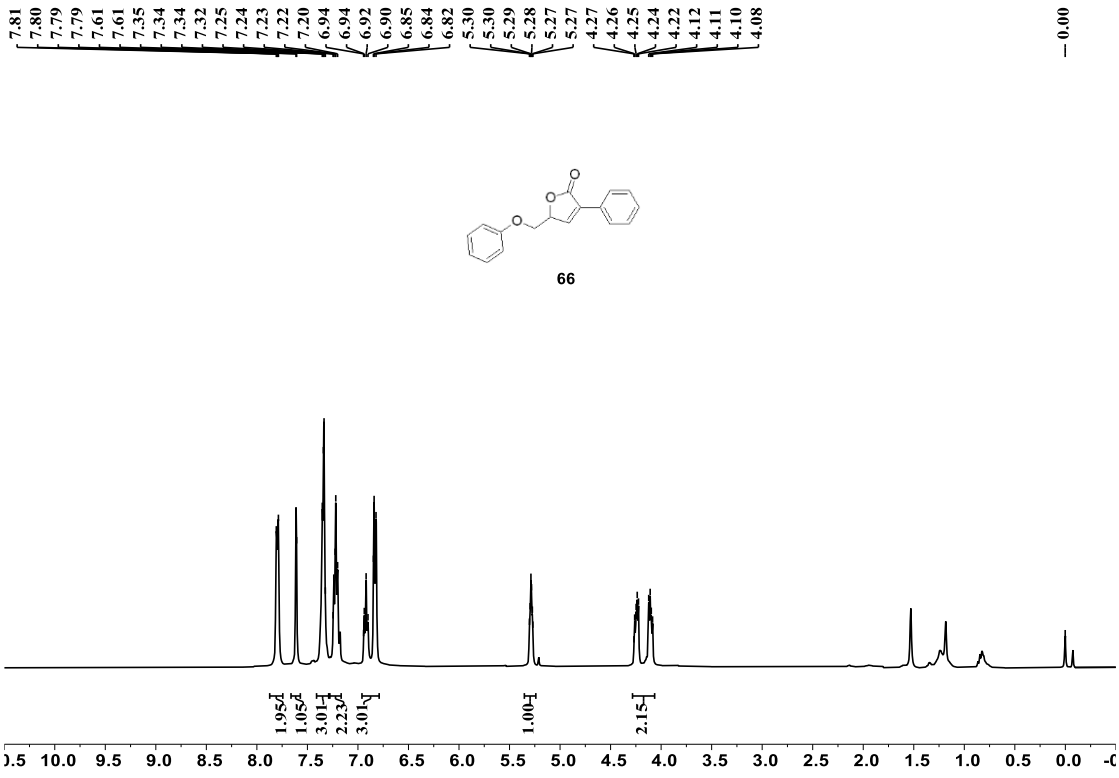

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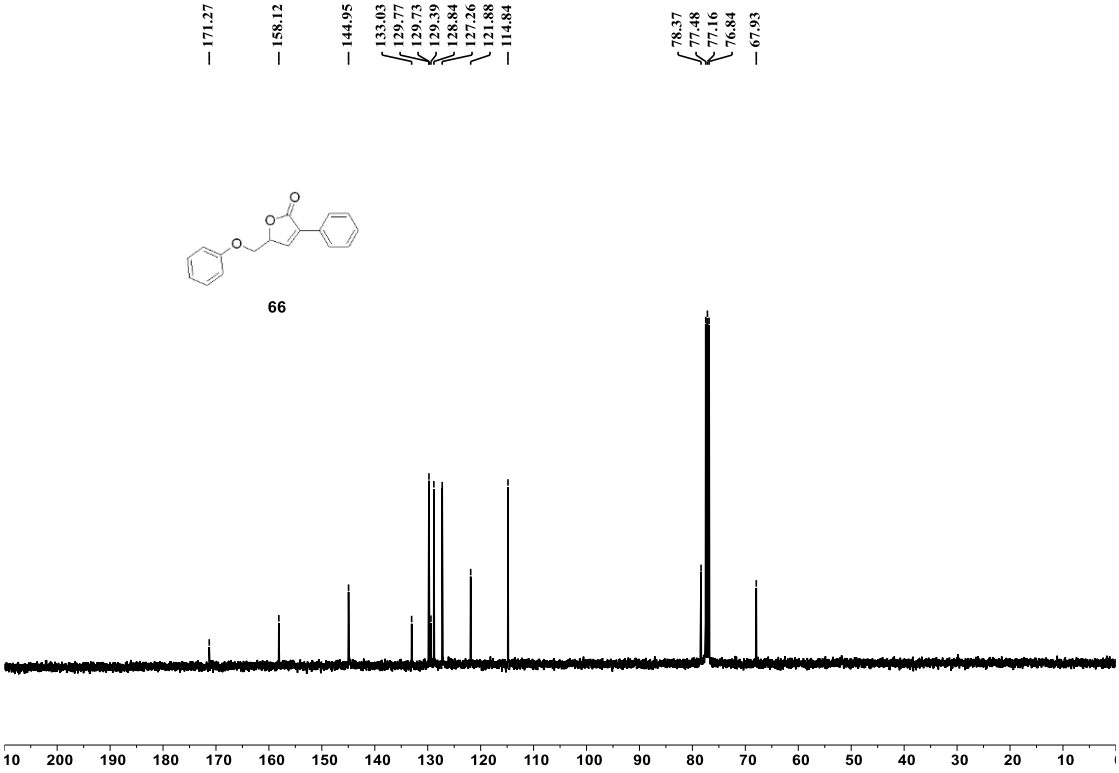

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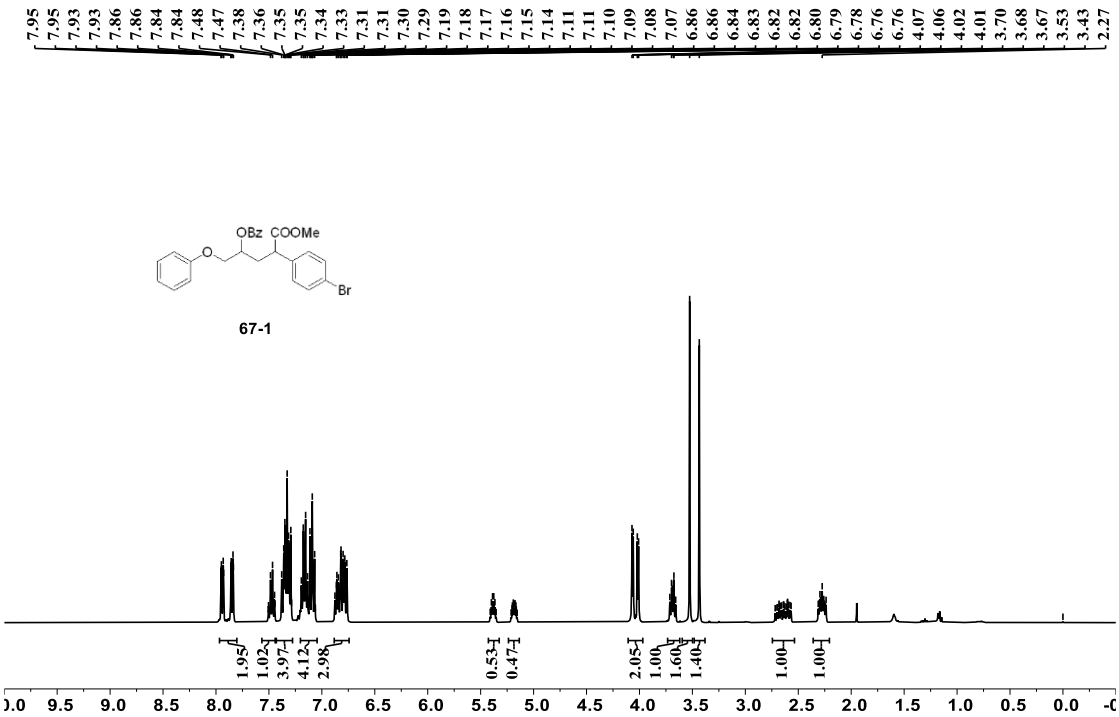

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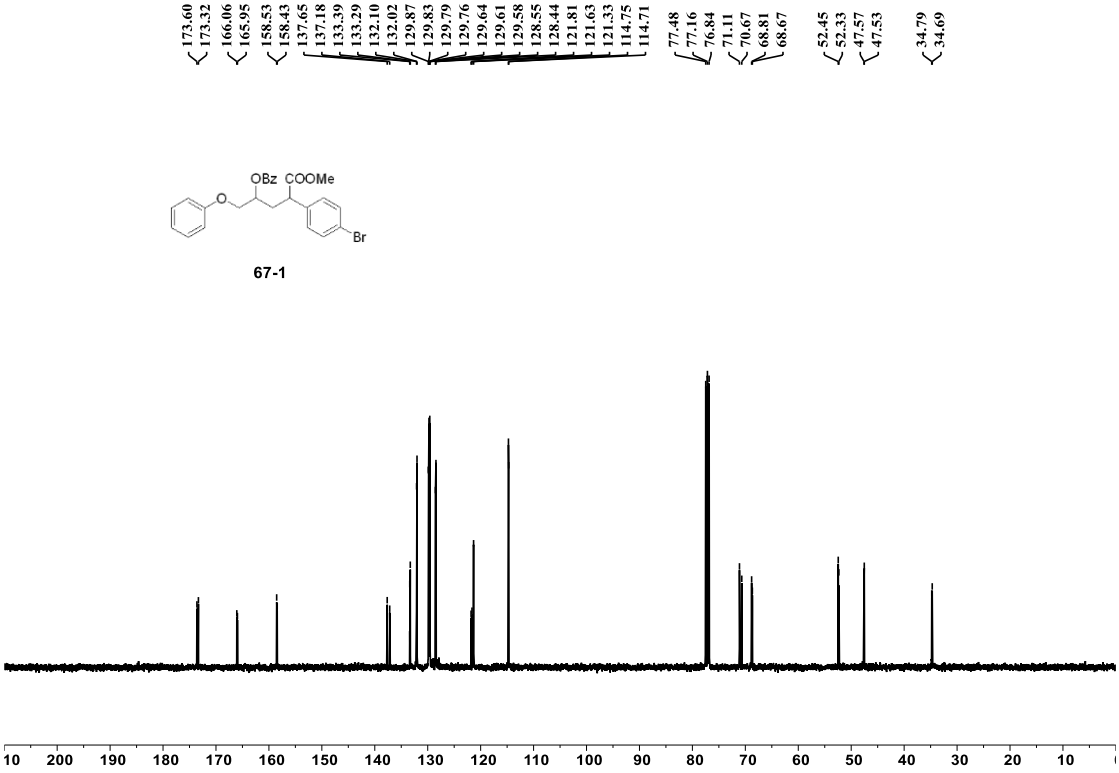

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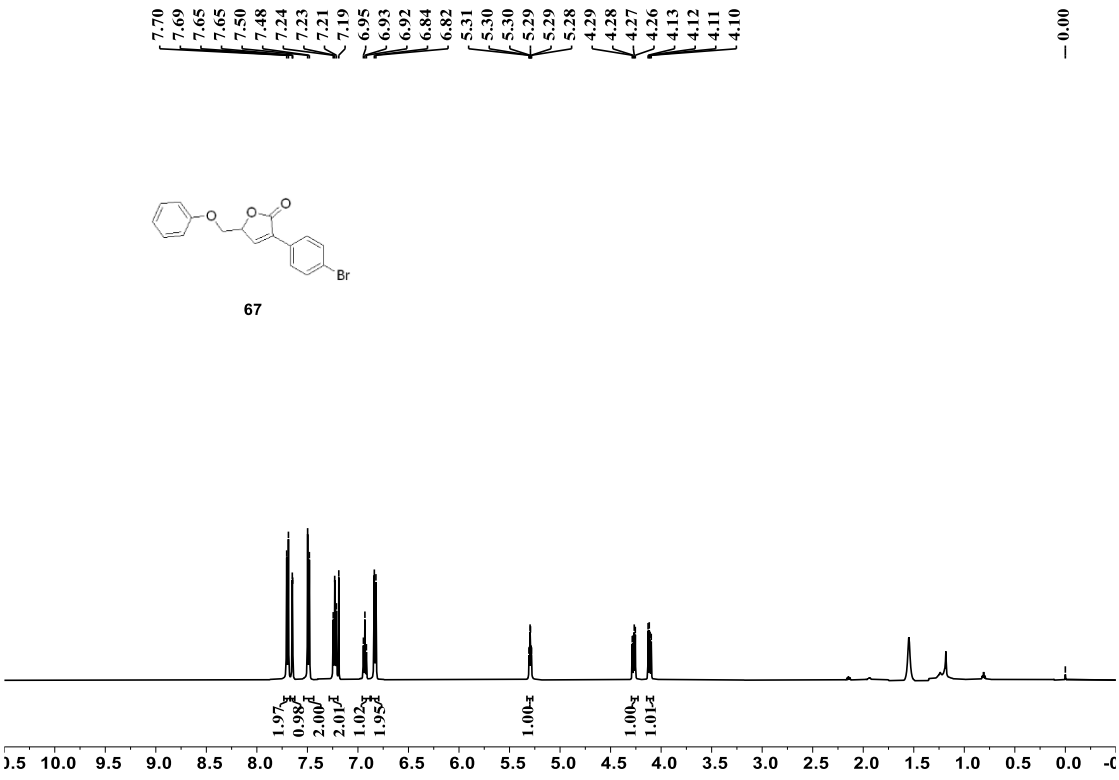

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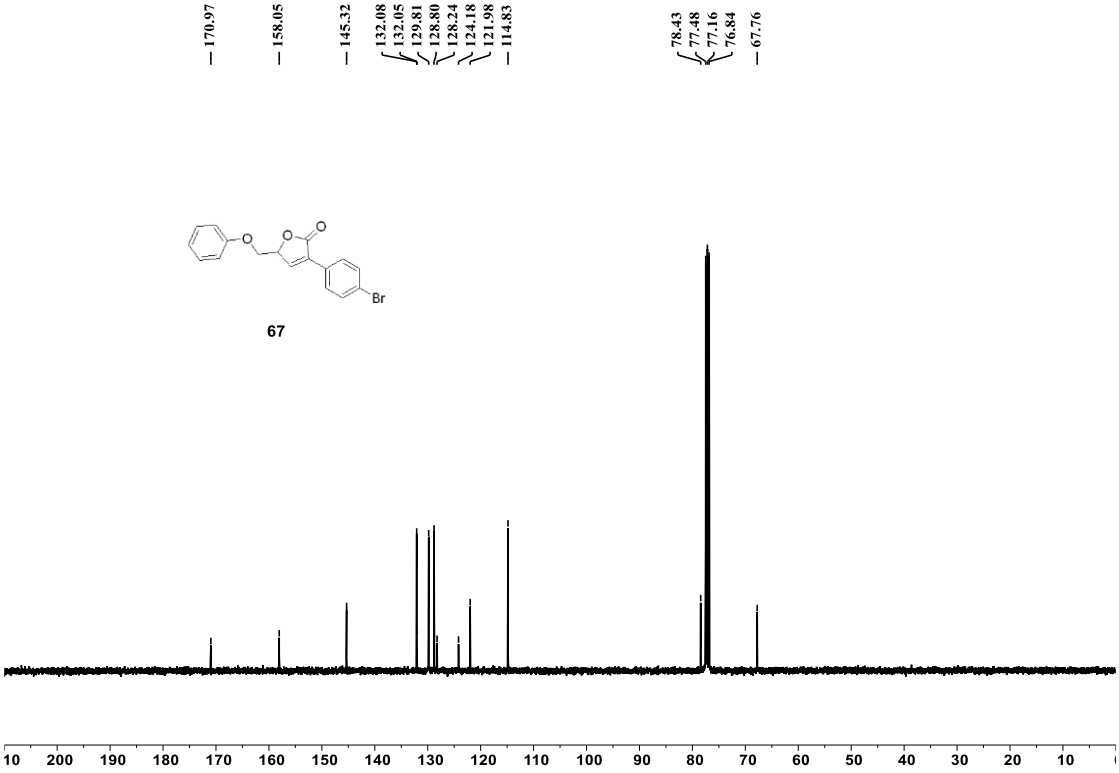

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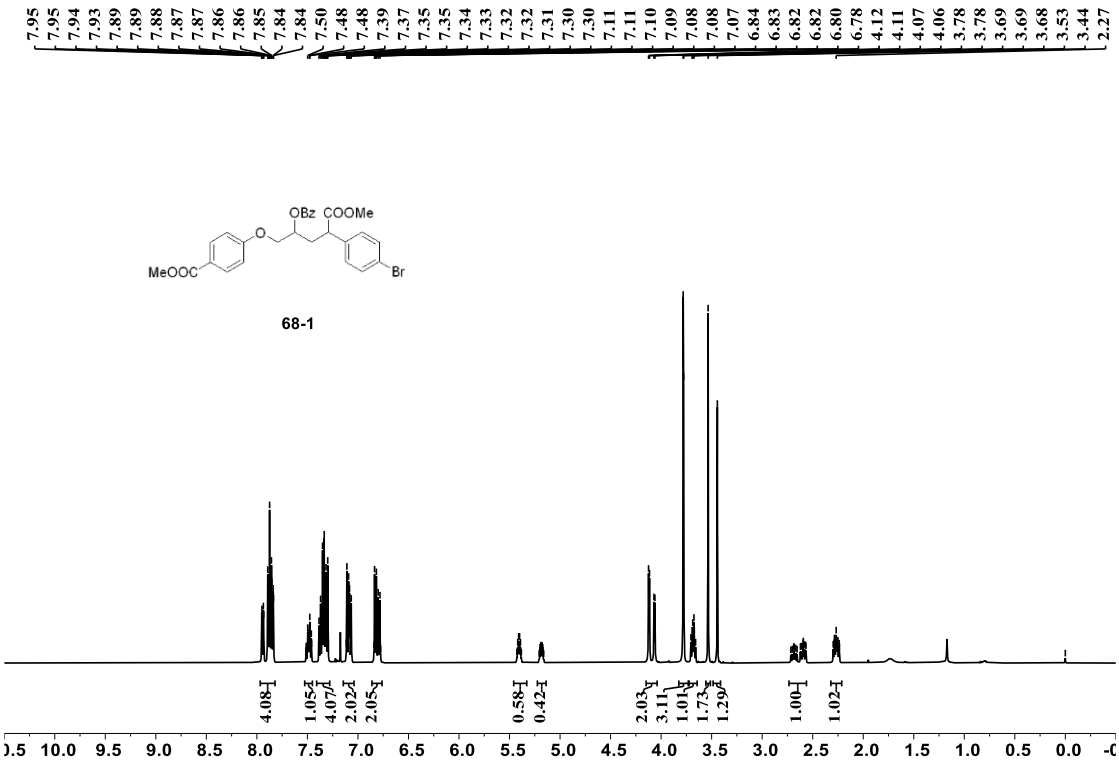

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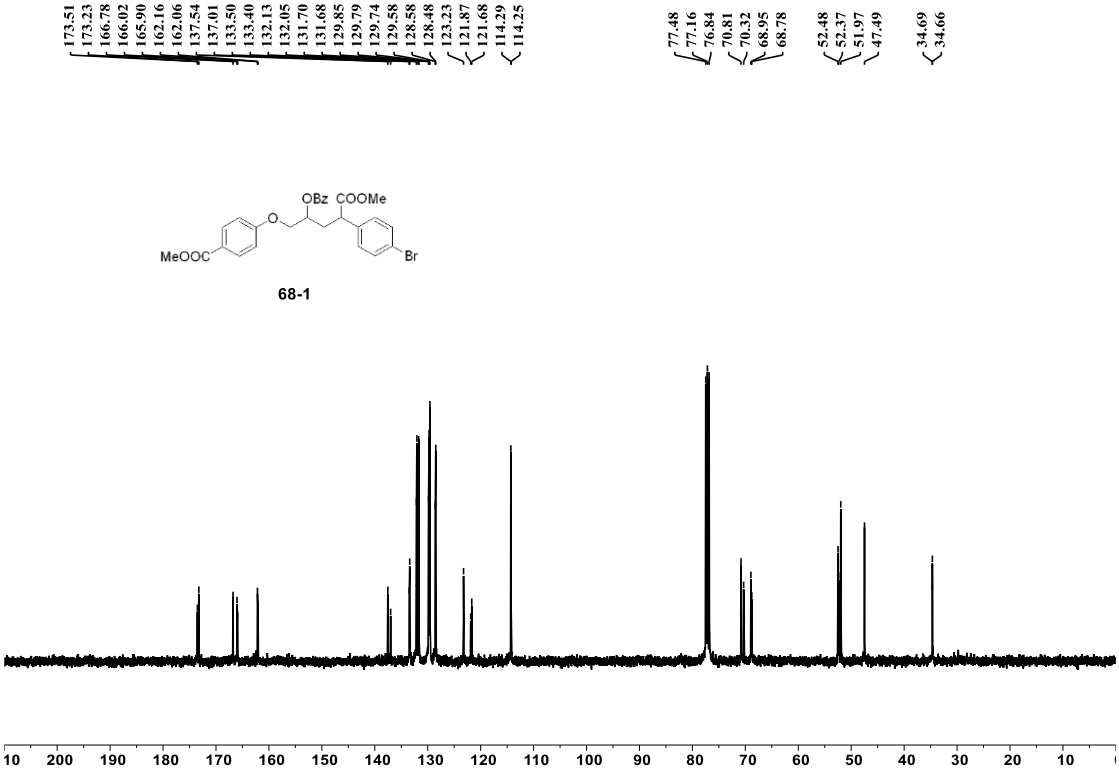

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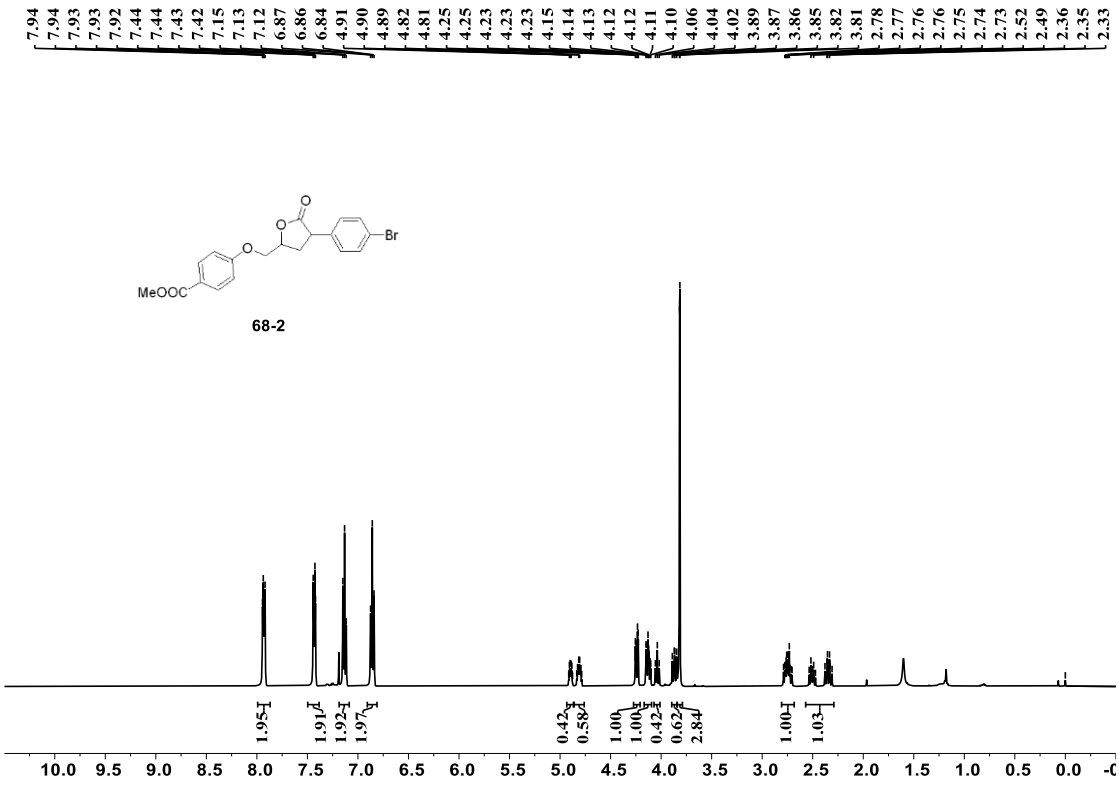

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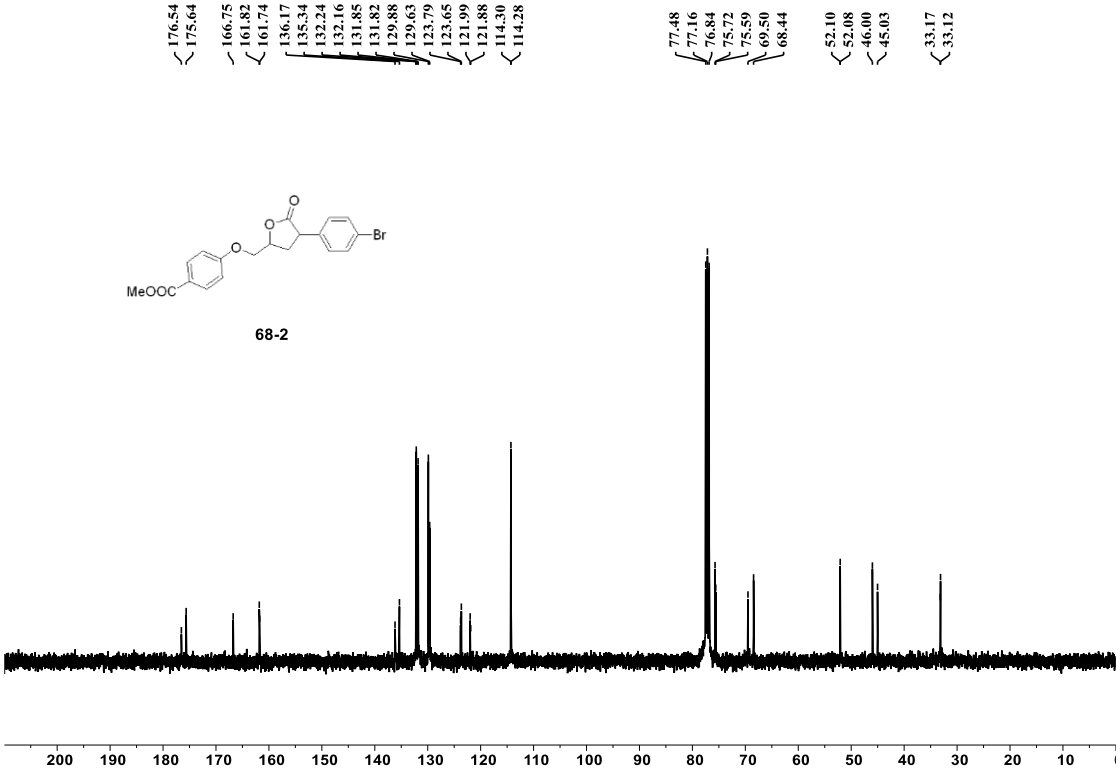

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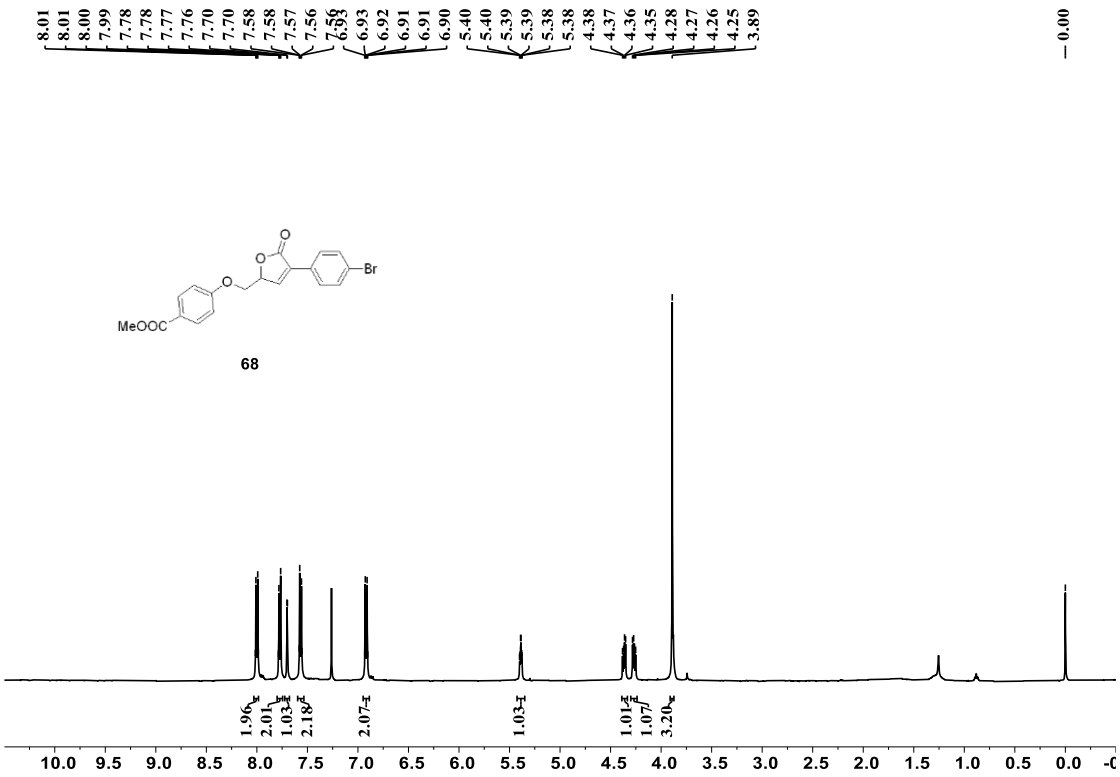

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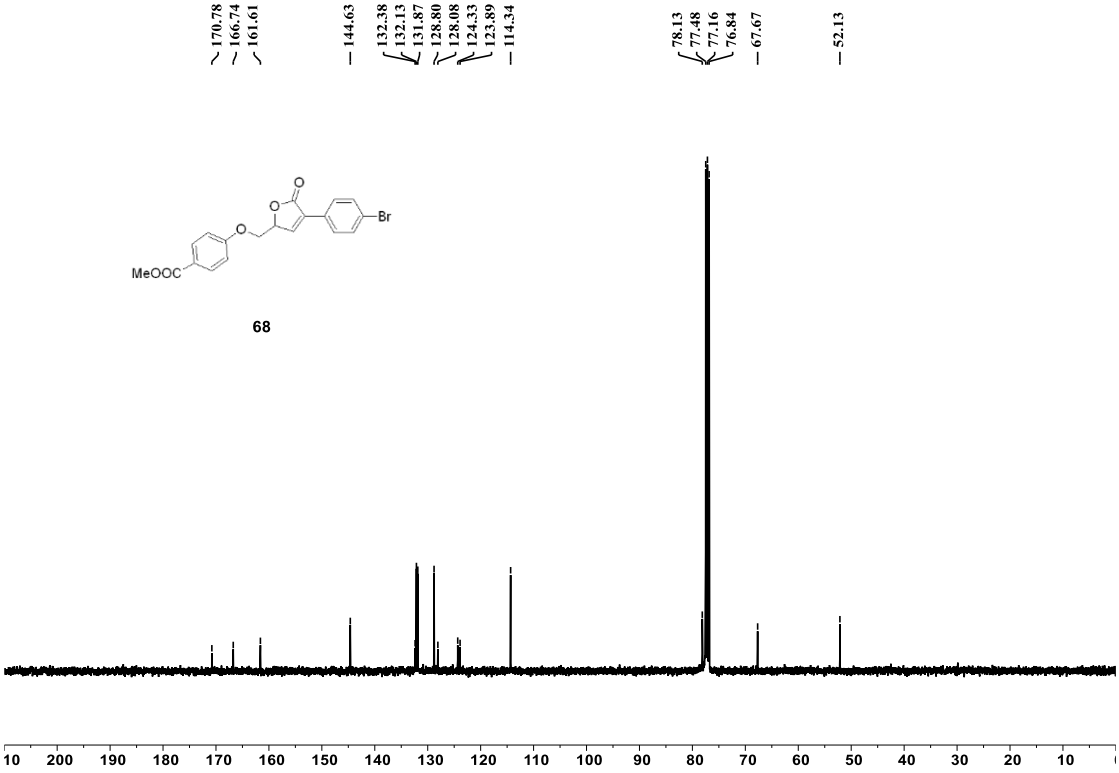

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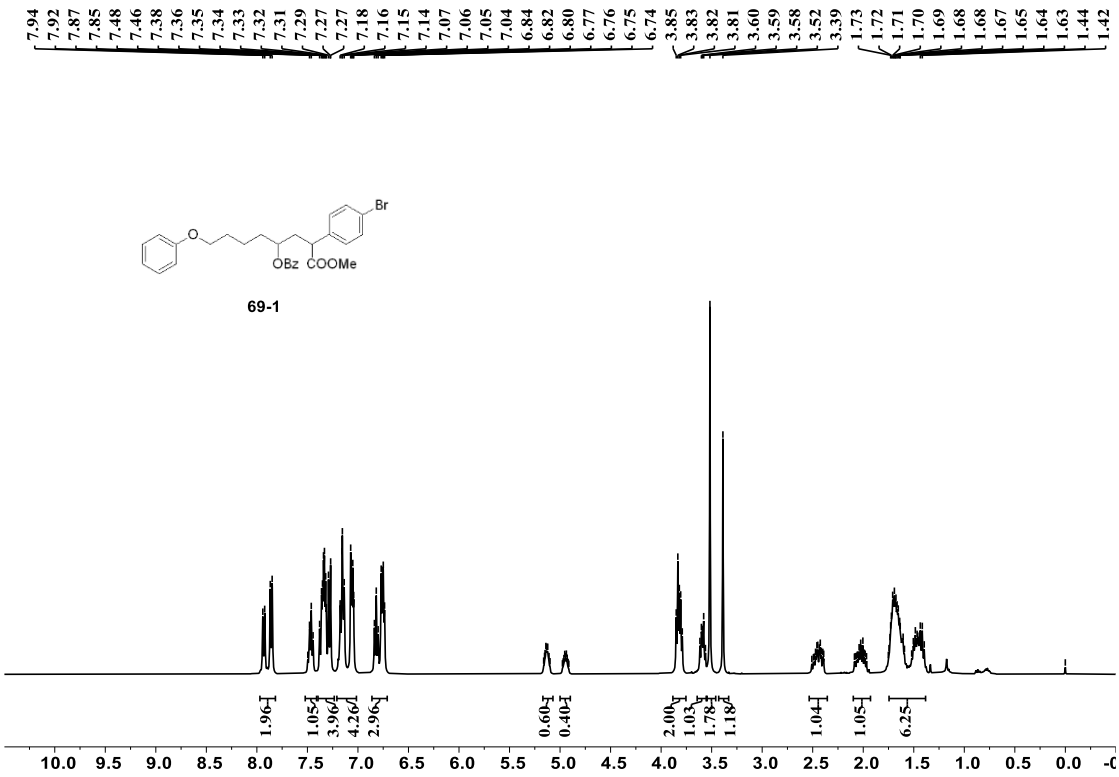

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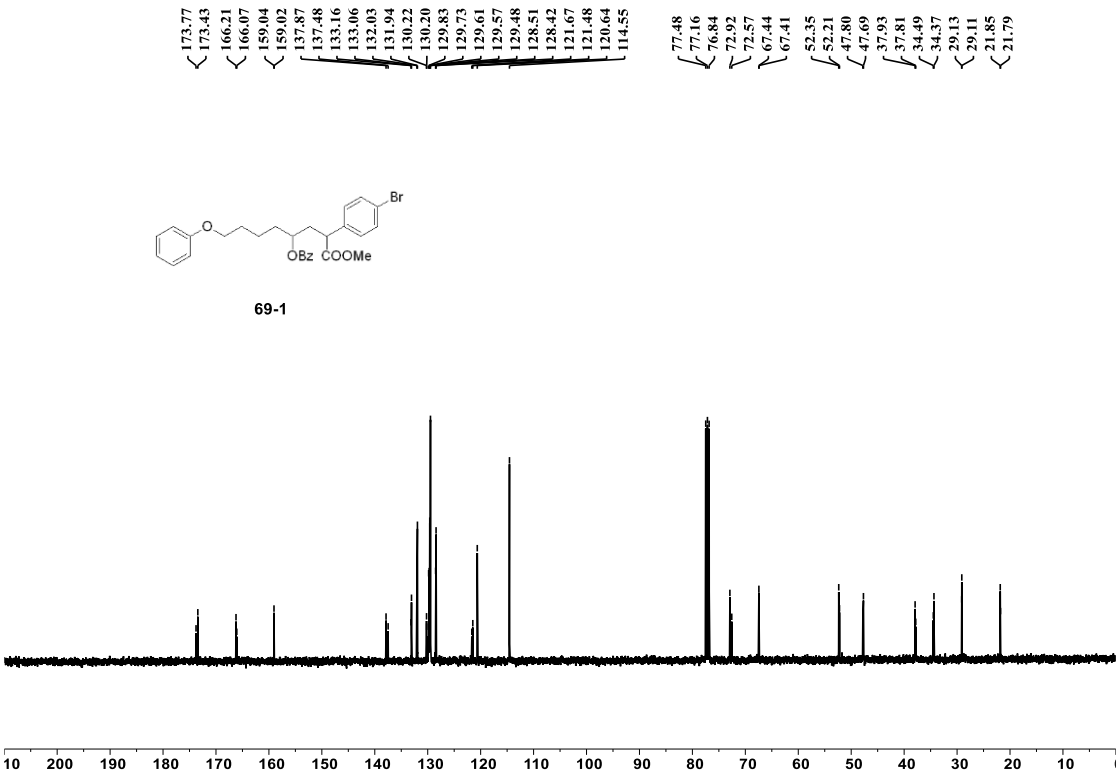

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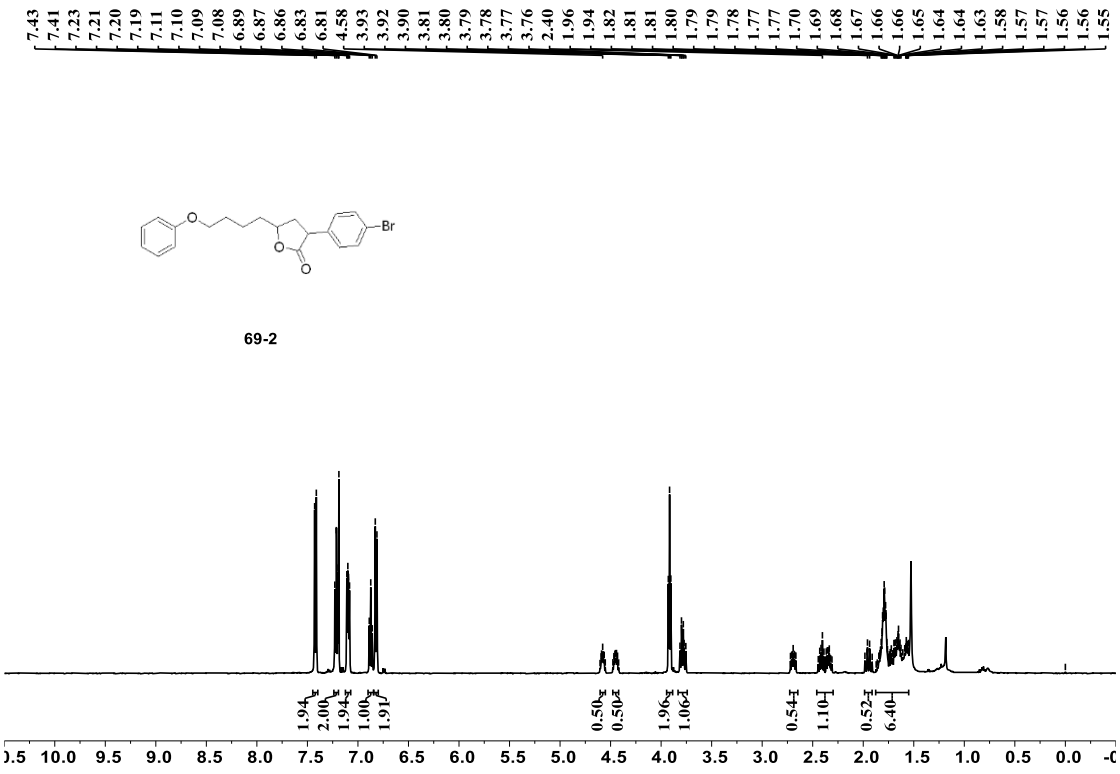

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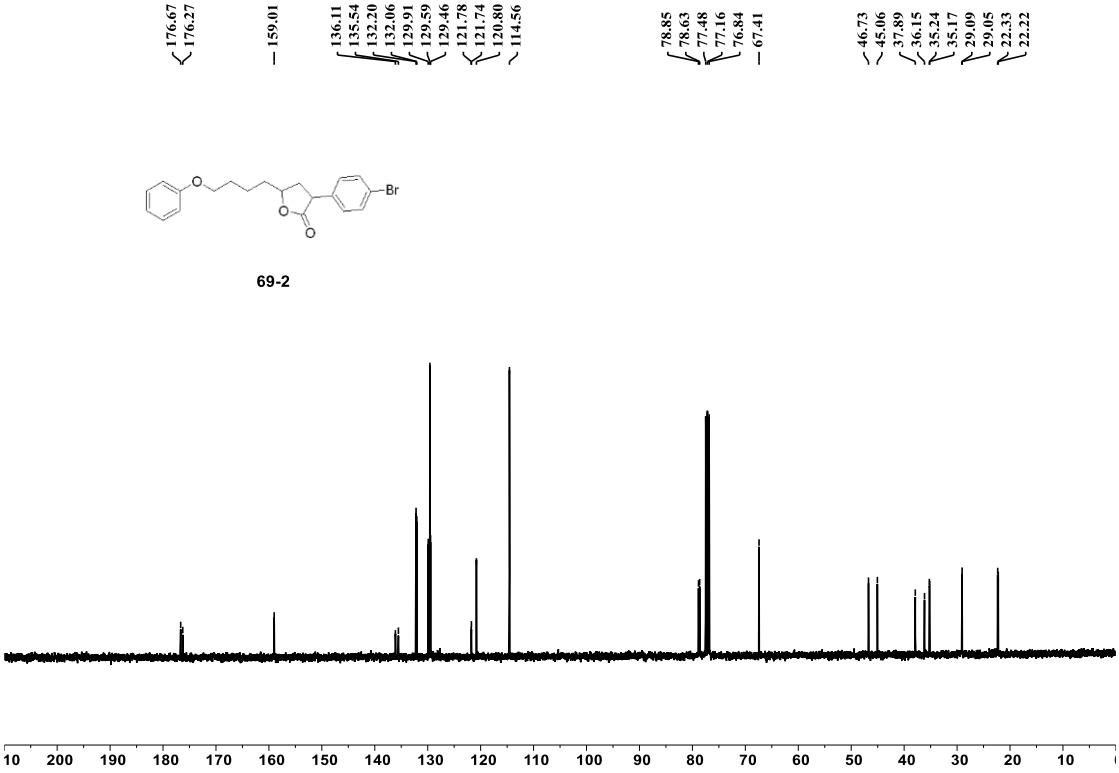

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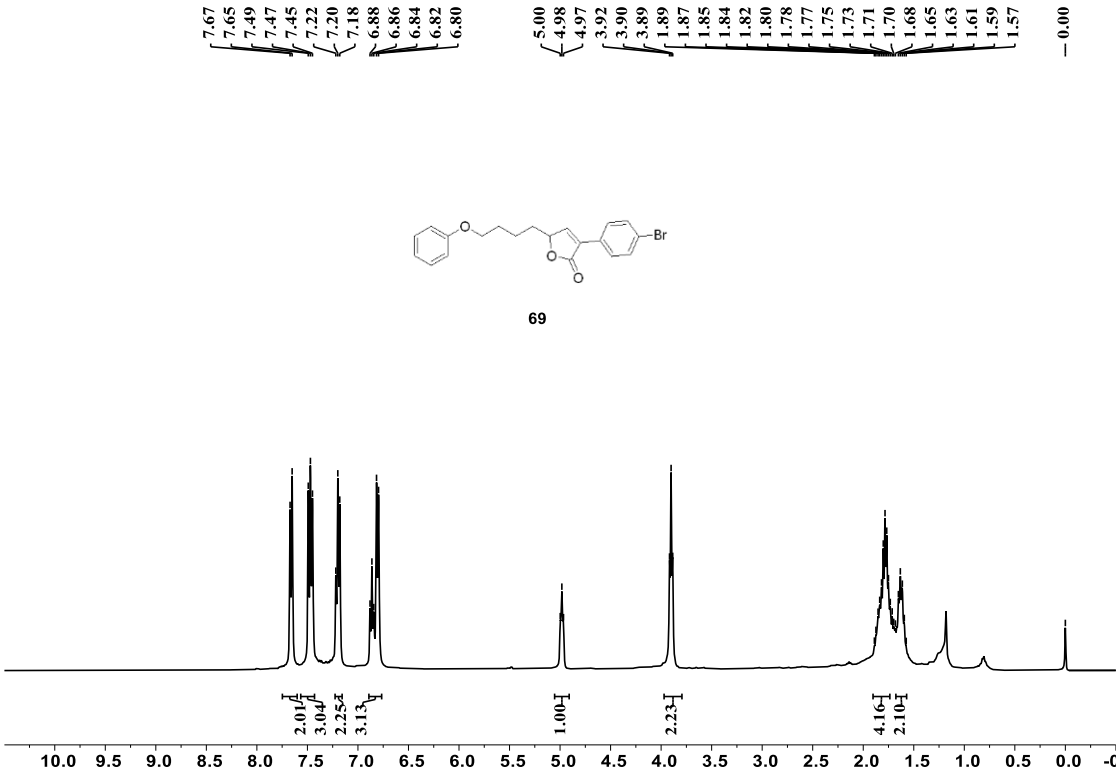

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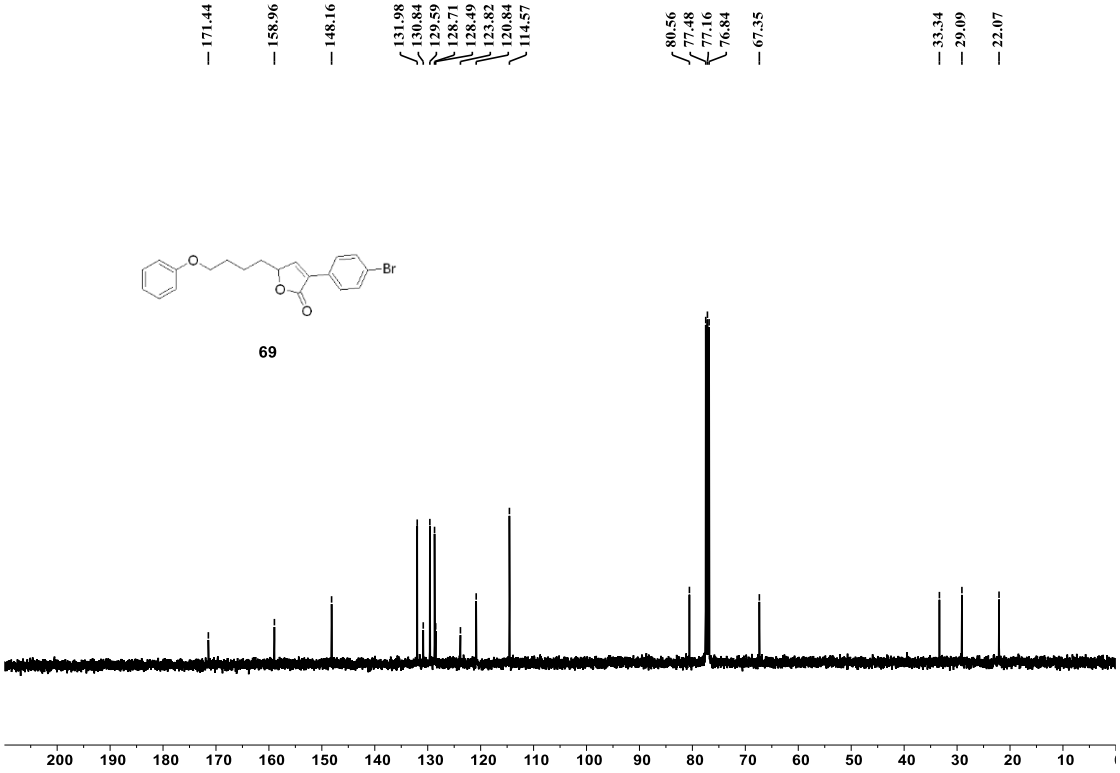

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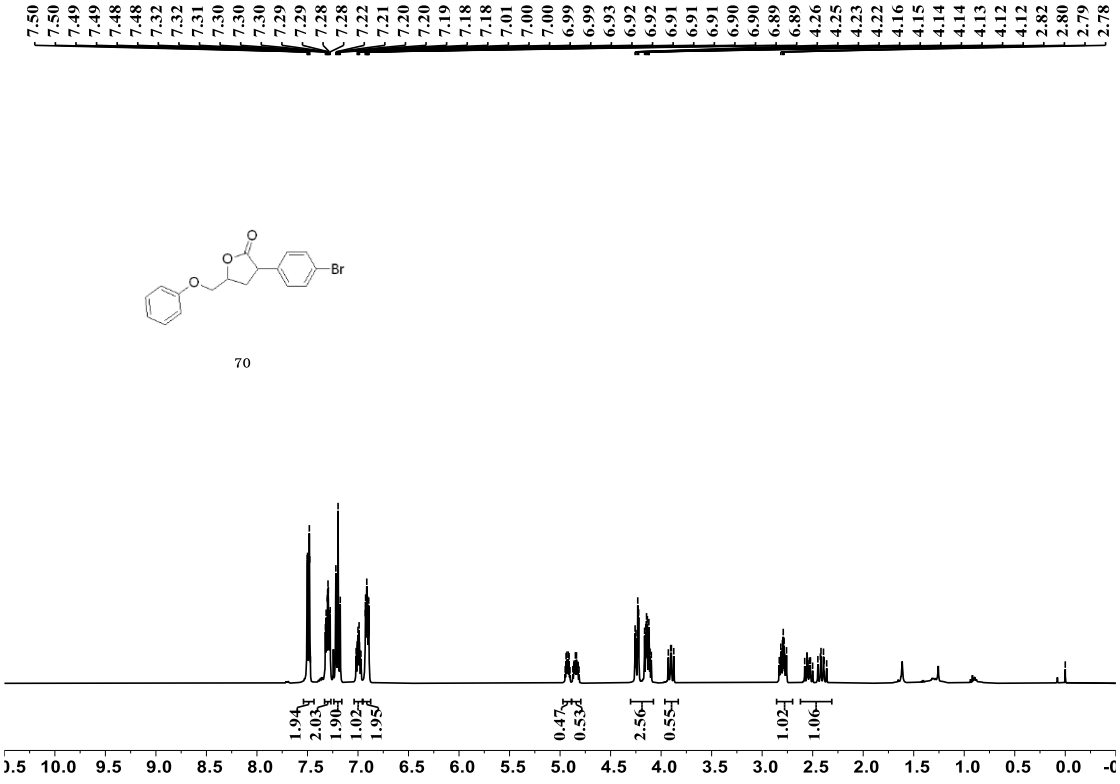

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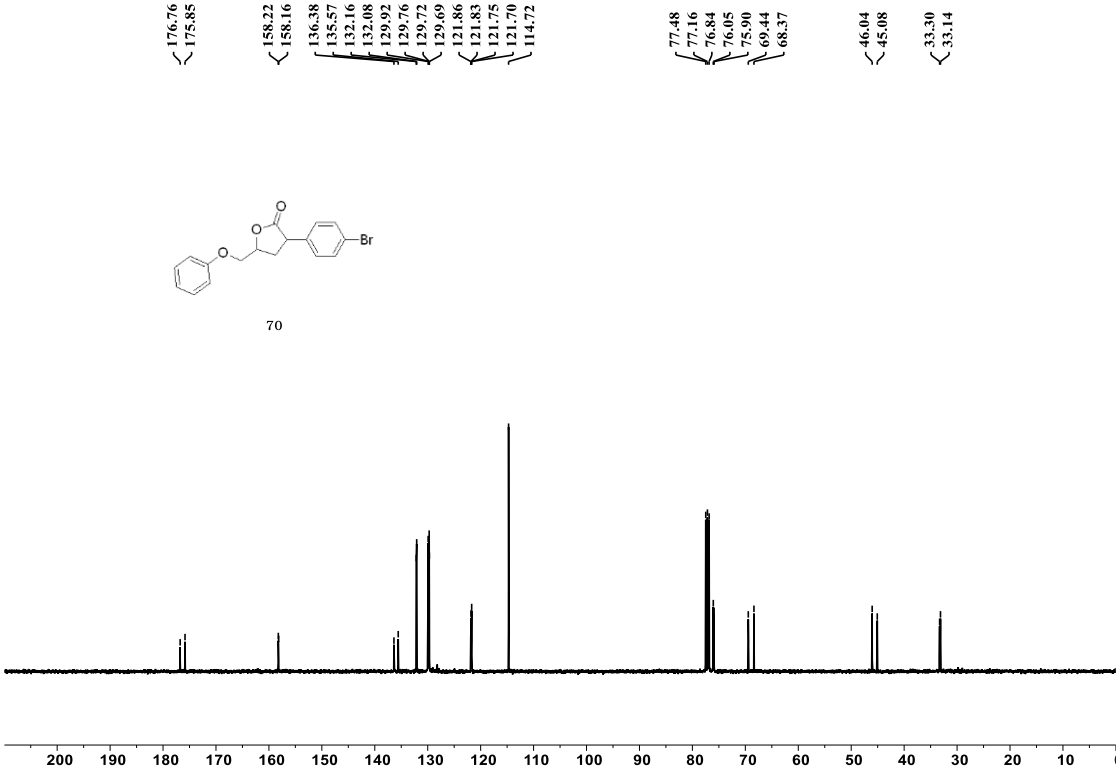

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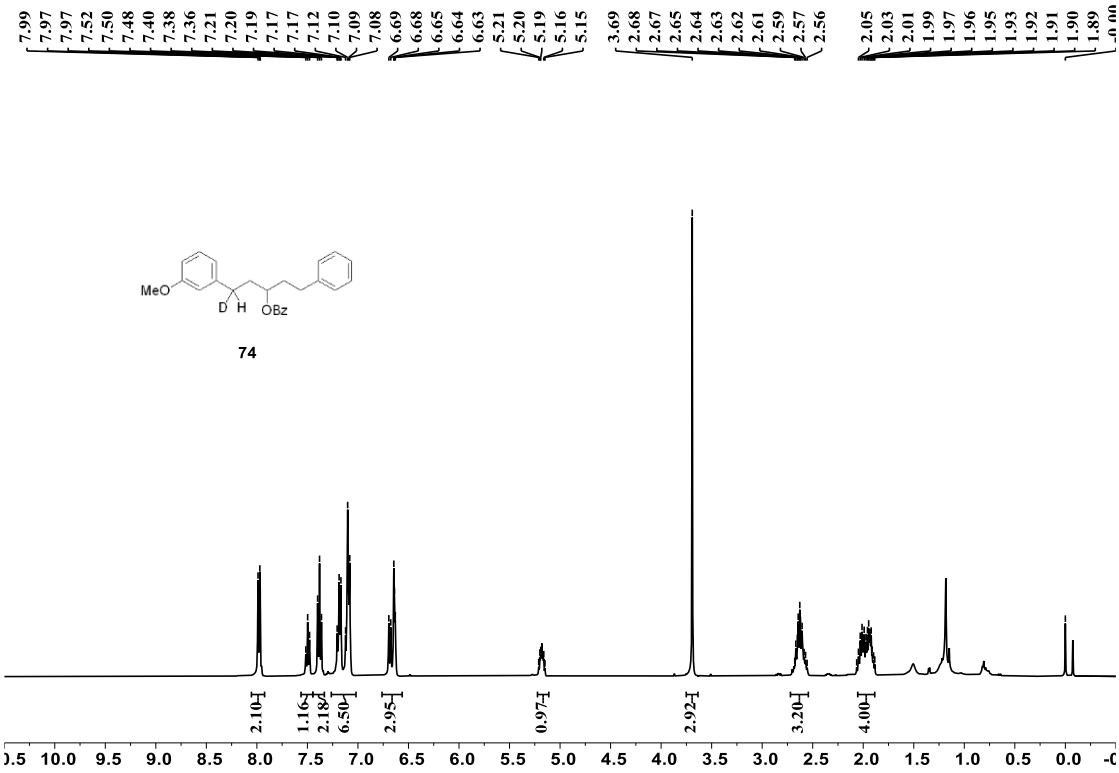

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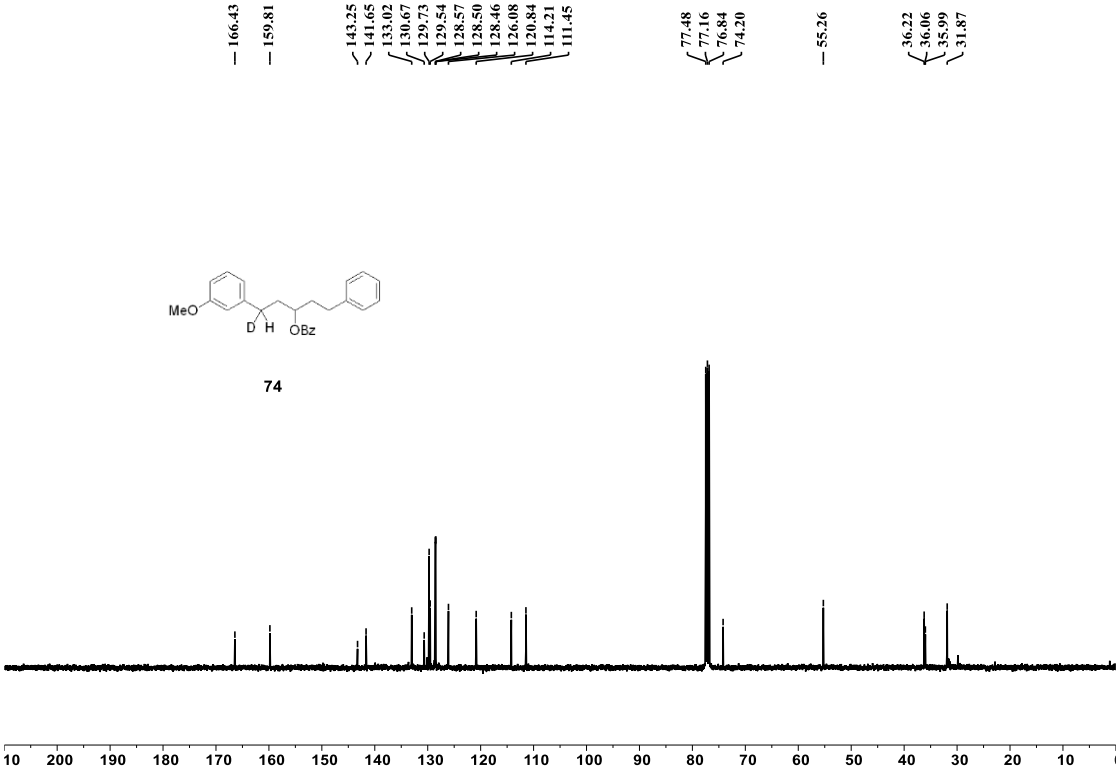
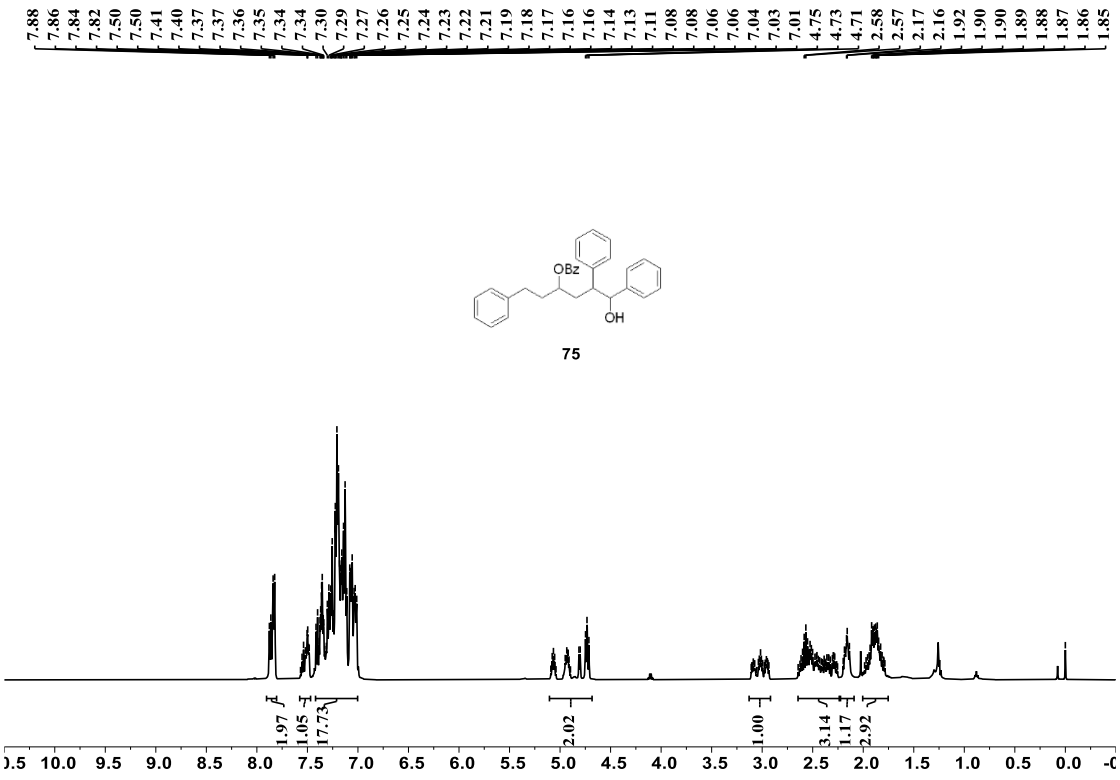


74

^{1}H NMR (500 MHz, $CDCl_3$)



75

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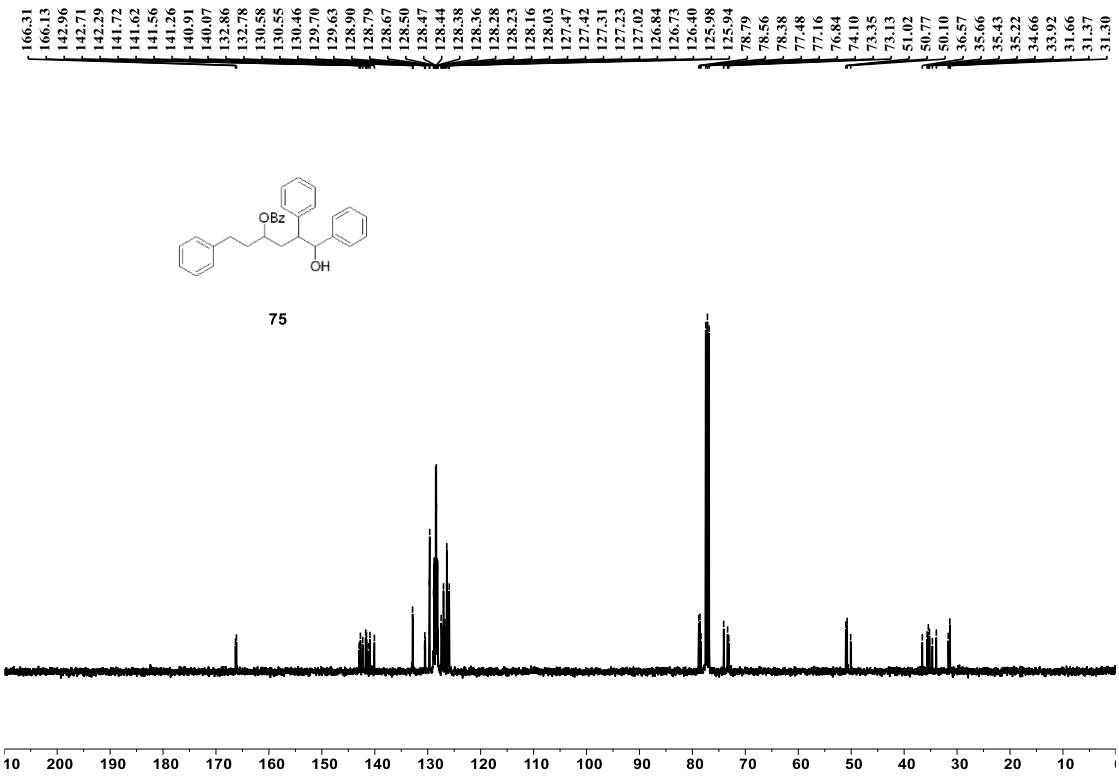

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